The self-consistent electron pairs method for multiconfiguration reference state functions

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Institut für Physikalische und Theoretische Chemie der Universität, D-6000 Frankfurt/M, West Germany

An efficient direct CI method which includes all singly and doubly substituted configurations with respect to an arbitrary multiconfiguration (MCSCF) reference function is described. The configurations are generated by subsequently applying spin-coupled two-particle annihilation and creation operators to the complete MCSCF function. This considerably reduces the size of the n-electron basis and the computational effort as compared to previous multireference CI treatments, in which the configurations are defined with respect to the individual reference configurations. The formalism of the method is very similar to the closed-shell "self-consistent electron pairs" (SCEP) method of Meyer. The vector $\mathbf{H}\,\mathbf{c}$ is obtained in terms of simple matrix operations involving coefficient and integral matrices. A full transformation of the two-electron integrals is not required. Test calculations with large basis sets have been performed for the $^3B_1$ and $^1A_1$ states of CH_2 ($\Delta E = 9.5$ kcal/mol) and for the $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$ reaction barrier ($\Delta E = 10.7$ kcal/mol). As a preliminary test for the accuracy of the results obtained with contracted wave functions of the above type the potential energy and dipole moment functions of the OH $X\,^2\Pi$ and $A\,^2\Sigma^+$ states have been calculated. For the $^2\Pi$ state r_e and ω_e deviate by less than 10^{-3} Å and 1 cm^{-1}, respectively, from the experimental data. For the $^2\Sigma^+$ state the agreement is somewhat less good, which is probably due to basis set defects. Around the equilibrium distance the calculated dipole moment functions are in very close agreement with those previously obtained from PNO–CEPA wave functions.

I. INTRODUCTION

During the last decade much progress has been made in the calculation of accurate electronic wave functions which cover a large fraction of the correlation energy. The computational methods used to treat this problem may be devided into two classes: (a) the conventional CI methods,[1–8] which involve the explicit construction and storage of the Hamilton matrix, and (b) the direct CI approaches,[9–13] which solve the Schrödinger equation iteratively without explicit construction of the Hamiltonian. The former methods have the advantage of being very general, i.e., any types of configurations may be included and excited state calculations present no particular problems. However, the size of the configuration expansion is quite limited, and therefore configuration selection schemes[2,3] or transformations to pair natural orbitals[4–8] often have to be performed. In the direct CI approaches, the vector $\mathbf{H}\mathbf{c}$, which is only needed for finding the desired eigenvector, is computed "directly" from the one and two electron integrals, so called "coupling coefficients," and the elements of the "trial vector" $\mathbf{c}$. This method has the advantage of being capable of treating much longer configuration expansions than the conventional CI methods.

The direct CI method, as developed by Roos,[10] was originally restricted to all single and double substitutions from a closed shell reference determinant. However, in order to treat excited states or to study the formation of chemical bonds, one often needs multiconfiguration (MCSCF) wave functions as the zeroth order approximation. In recent years the convergence with MCSCF methods has been much improved and MCSCF wave functions are now routinely available.[14] In many cases very accurate results can be obtained at just the MCSCF level.[15–19] However, the reliability of the results often depends crucially on the configuration and/or orbital spaces considered. In order to remove such uncertainties the development of efficient CI methods, which include all single and double substitutions with respect to an arbitrary MCSCF type reference function, is a commonly accepted goal.

Recently, several generalizations of the direct CI method to one open shell[20,21] or several closed shell[22] reference configurations have been described. Using the graphical unitary group approach (GUGA) developed by Paldus[23] and Shavitt,[24] Siegbahn generalized the direct CI method for arbitrary multiconfiguration reference state functions.[25] Other MR–CI methods have recently been described by Buenker and Peyerimhoff,[2,3] Brooks and Schaefer,[26,27] Duch and Karwowski,[28] Duch,[29] Tavan and Schulten,[30] Taylor,[8] Liu and Yoshimine[31] and Lischka et al.[32] Much of this recent progress is due to the realization that for the case of wave functions with at most two electrons in the external orbital space, the coupling coefficients can always be factorized into a complicated but relatively small set of "internal coefficients" and a large but very simple set of "external coefficients" which do not have to be stored.[24,25] That this is true for wave functions which include double substitutions from a multiconfiguration reference function has been shown earlier in a slightly different context by Meyer.[4]

The common feature of the above MR–CI treatments is that they include all singles and doubles which can be generated from several reference configurations. This leads to rapidly growing configuration expansions as the number of reference configurations increases. An alternative to this ansatz for the case of MCSCF reference functions has first been proposed by Meyer.[4] Instead of including all single and double substitutions with respect to the individual reference configurations one

may generate the doubly substituted configurations by subsequently applying spin-coupled two-particle annihilation and creation operators to the complete MCSCF function. In this way those configurations which arise from different reference configurations by applying the same operators are contracted with appropriate coefficients. Furthermore, it has been shown[4] that by using the pair annihilation and creation operators only such configurations are generated which belong to the "first order interacting space"[33,34] of the reference function. These facts often considerably reduce the length of the configuration expansion. Most important in this context is that for a given set of M correlated internal orbitals the number n_p of linearly independent pair functions is always $\leq M^2$ and, in contrast to the more general MR–CI case, essentially independent of the number of reference configurations. This may drastically reduce the computational effort, since the number of operations required for the two most expensive steps of any direct CI approach is proportional to $n_p N^4$ and $\sim n_p^2 N^3$, where N is the number of external orbitals. As will be demonstrated in Sec. V, the approximation of generating the configurations from a contracted reference function seems to have very little influence on the accuracy of the results. In fact, the "contracted multiconfiguration reference–CI" (CMR–CI) wave functions differ from the corresponding uncontracted MR–CI wave functions only by relatively unimportant second order terms, and therefore, virtually the same results are to be expected for both cases, provided the reference function properly approximates the state under consideration. Only in cases where two internal states are nearly degenerate and have a different electronic structure—as is, for instance, the case near avoided crossings—an appreciable change of the contraction coefficients through electron correlation effects is to be expected. One can easily account for this effect, however, by relaxing the coefficients during the iteration process. This will be investigated in some detail in a separate publication. We note that a direct CI formalism based on the CMR–CI ansatz has recently also been described by Siegbahn.[35] However, in this treatment the important semi-internal configurations were not accounted for and no numerical results were given.

Most CI methods described in the literature require a full transformation of the two-electron integrals into MO basis as a first step. Although this seems to be no longer a bottleneck for relatively small basis sets, the transformation time ($\sim N^5$) becomes comparable to the remaining time ($\sim N^4$) for about 50–70 basis functions in the largest symmetry block. Therefore, various schemes have been proposed which avoid the full integral transformation.[11,12,36] A particlarly simple and efficient approach is the "self consistent electron pairs" (SCEP) method of Meyer.[11] The SCEP method is in principle a direct CI, i.e., the explicit construction of the Hamilton matrix is avoided. However, the structure of the formalism and the computational process is quite different from the original direct CI method.[9,10] In the latter the individual integrals are handled together with the appropriate coupling and CI coefficients and the full CI vector has to be kept in high speed memory. On the other hand, in the SCEP method, those coefficients

which can always be treated with the same internal coupling coefficients are grouped into matrices and vectors. By a particular normalization of the doubly substituted configurations the "external" coupling coefficients are removed entirely. The elements of the vector $\mathbf{Hc}$ are then obtained in terms of simple matrix operations involving the coefficient matrices and generalized Coulomb and exchange operators, which represent the two-electron integrals with at least two internal orbitals in a particular order. The contributions of the integrals with three and four external orbitals are included by calculating one external exchange operator per pair iteration. At the expense of four matrix multiplications per pair per iteration, these operators can be obtained directly from the two electron integrals in AO basis, thus avoiding the full integral transformation. This is most advantageous for calculations with large basis sets and not too many pairs. Since only four matrices have to be held simultaneously in high speed memory, large scale SCEP calculations can easily be performed even on minicomputers with a small amount of available central memory. On the other hand, the matrix formalism is optimally suited for the use of modern supercomputers with efficient array processors. We may note in this place that some of the characteristic features of the SCEP method, e.g., the use of integral matrices and externally singlet and triplet coupled configurations, have also been adopted in the most recent direct-CI methods of Siegbahn.[25,35]

The SCEP method was originally restricted to all single and double substitutions with respect to one closed shell reference determinant. It has been programmed and applied by Dykstra,[11] Werner and Reinsch,[37] and Zirz and Ahlrichs.[38] Dykstra[39] has reformulated the SCEP theory for certain types of openshell wave functions and for GVB reference state functions which consist only of closed shell determinants. However, in both cases the semi-internal configurations were left out. Recently, Flesch and Meyer[40] have generalized the SCEP procedure for a spin-unrestricted open-shell reference determinant (UHF–SCEP).

In this paper we will describe the generalization of the SCEP method for arbitrary multiconfiguration reference functions. For the reasons discussed above we will define the configuration state functions with respect to a contracted reference function (CMR-SCEP), but only very minor changes of the formalism are necessary to generalize it to the uncontracted MR–SCEP case. Very similar to the closed shell SCEP method our approach is based on simple matrix operations. The main difference lies in the fact that the internal Coulomb and exchange operators do not enter with fixed coefficients but rather have to be linearly combined with precalculated factors. These factors, which may be regarded as "internal coupling coefficients," depend only on the structure of the reference function. Therefore, their number is relatively small and independent of the size of the basis set. They will be explicitly given in terms of overlap and transition density matrix elements between a set of "core functions"[4] which are obtained by deleting one or two internally spin coupled electrons from the reference function. This makes

possible evaluating all factors quite quickly even without techniques such as the unitary group approach.

In Sec. II we describe in some detail the construction of the orthogonal set of configuration state functions. In Sec. III the formulas for the Hamilton matrix elements are given and the iteration process is described. Some computational aspects and possible extensions of the method are discussed in Sec. IV, and finally in Sec. V some numerical results are presented. It will be shown, that the efficiency of our method compares very favorably with other MR–CI methods recently described in the literature and that with CMR–CI wave functions highly accurate results can be obtained.

II. CONSTRUCTION OF THE CONFIGURATION STATE FUNCTIONS

As is common practice, the wave function is expanded in an n-particle basis of orthogonal, spin (and possibly symmetry) adapted configuration state functions (CSF's) $\{\Psi\}$. The CSF's are constructed from an orthonormal set of molecular orbitals. In the following we shall denote those orbitals which are occupied in any of the reference configurations "internal orbitals" (labeled by $i, j, \ldots$) and the remaining ones "external orbitals" ($a, b, \ldots$). The internal orbital space may further be devided into a set of "core" orbitals, which are doubly occupied in any of the reference configurations and not correlated, and the remaining set of "valence" orbitals. In the following the indices $i, j, k, \ldots$, will denote valence orbitals only, and the corresponding summations are over this subspace only. The indices $r, s \ldots$ run over valence and external orbitals.

The total wave function may be devided into four parts

$$\Psi = \Psi_0 + \sum_I c_I \Psi_I + \sum_S \sum_a c_S^a \Psi_S^a + \sum_P \sum_{ab} C_P^{ab} \Psi_P^{ab} \ , \quad (1)$$

where

$$\Psi_0 = \sum_k a_k \Psi_k^{ref} \quad (2)$$

is the reference state function, which may be composed of several configurations Ψ_k^{ref}. The coefficients a_k and the internal orbitals are usually optimized in a preceding MCSCF calculation. The internally excited configurations Ψ_I, the singly excited and semi-internal doubly excited configurations Ψ_S^a, and the doubly external congiruations Ψ_P^{ab} have zero, one, and two electrons, respectively, in the external subspace.

As has been extensively discussed elsewhere[4,33,34] the configuration basis should exactly span the "first order interacting space" of the reference state function. It has been shown by Meyer[4] that such a basis can be obtained by subsequently applying spin-coupled pair annihilation and creation operators $\hat{B}$ and $\hat{B}^+$, respectively, to the reference function Ψ_0

$$\Psi_{ijp}^{rs} = 1/\sqrt{2} \sum_m \hat{B}_{rspm}^+ \hat{B}_{ijpm} \sum_k a_k \Psi_k^{ref} \ , \quad (3)$$

with

$$\hat{B}_{ijpm} = \begin{cases} \eta_i \, \eta_j \ , & p = -1 \ , & m = 1 \ , \\ 1/\sqrt{2}(\eta_i \bar{\eta}_j + p \, \eta_j \bar{\eta}_i) \ , & p = \pm 1 \ , & m = 0 \ , \quad (4) \\ \bar{\eta}_i \, \bar{\eta}_j \ , & p = -1 \ , & m = 1 \ . \end{cases}$$

$p = 1 - 2s$ denotes singlet ($p = 1$) and triplet ($p = -1$) pairs and η_i are the usual spin–orbital annihilation operators. According to the spin-coupling in Eqs. (3) and (4) the configurations Ψ_{ijp}^{rs} are always spin–eigenfunctions, provided the same is true for Ψ_0. However, in general, the Ψ_{ijp}^{rs} are not orthonormal and often not even linearly independent. For the doubly external configurations the elements of the metric matrix are given by

$$\langle \Psi_{ijp}^{ab} | \Psi_{klq}^{cd} \rangle = \tfrac{1}{2} (\delta_{ac} \, \delta_{bd} + p \delta_{ad} \, \delta_{bc}) \, \delta_{pq} \sum_m \langle \Phi_{ijpm} | \Phi_{klqm} \rangle \ , \quad (5)$$

where

$$\Phi_{ijpm} = \hat{B}_{ijpm} \Psi_0 \ . \quad (6)$$

Hence, in order to orthogonalize the configurations one has just to transform a linearly independent subset of the $n-2$ electron core functions[4] Φ_{ijpm} into a new set Φ_{Ppm}

$$\Phi_{Ppm} = \sum_{i \geq j} A_{P,ij}^{(p)} \Phi_{ijpm} \ ,$$

such that

$$\langle \Phi_{Ppm} | \Phi_{Qpm} \rangle = \sum_{i \geq j} \sum_{k \geq l} A_{P,ij}^{(p)} A_{Q,kl}^{(p)} \sum_m \langle \Phi_{ijpm} | \Phi_{klpm} \rangle = \delta_{PQ} \quad (7)$$

is valid. Since the final wave function is invariant to a unitary transformation of the Φ_{Ppm}, the transformation matrices $A^{(p)}$ can be found by any of the usual orthogonalization procedures. It is to be noted, that different transformations are performed for singlet ($p = 1$) and triplet ($p = -1$) pairs, but in order to retain spin adapted configurations the same transformation has to be performed for all three components ($m = 0, \pm 1$) in the triplet case. For simplicity, in the following the spin index p is considered as part of the pair label P. The orthogonal doubly external configurations are now obtained as

$$\Psi_P^{ab} = 1/\sqrt{2} \sum_m \hat{B}_{abpm}^+ \Phi_{Pm} \ . \quad (8)$$

According to this definition only the "diagonal" configurations are normalized $\langle \Psi_P^{aa} | \Psi_P^{aa} \rangle = 1$, whereas $\langle \Psi_P^{ab} | \Psi_P^{ab} \rangle = \tfrac{1}{2} (a \neq b)$. This particular normalization makes possible the simple matrix formalism in the next section, since all external coupling coefficients become unity. We may now define "pair functions"

$$\Psi_P = \sum_{ab} C_P^{ab} \Psi_P^{ab} \ , \quad C_P^{ab} = p C_P^{ab} \ , \quad (9)$$

which are represented by the symmetric (singlet pairs) or antisymmetric (triplet pairs) coefficient matrices C_P.

Quite analogously to the doubly external configurations we define the semi-internal (and singly excited) configuration space. Again we first construct a set of $n - 1$ electron core functions

$$\Phi^{k}_{ijp,m} = \begin{cases} (1-p)/2\,\eta^{*}_{k}\Phi_{ijp,1} + 1/\sqrt{2}\,\overline{\eta}^{*}_{k}\Phi_{ijp,0}\,, & m=1/2\,, \\ (1-p)/2\,\overline{\eta}^{*}_{k}\Phi_{ijp,-1} - p/\sqrt{2}\,\eta^{*}_{k}\Phi_{ijp,0}\,, & m=-1/2\,. \end{cases}$$
(10)

A linearly independent subset of these functions is then orthonormalized according to the condition

$$\sum_{m=-1/2}^{1/2} \langle \Phi_{Sm} | \Phi_{Tm} \rangle = \delta_{ST}$$
(11)

and the spin-adapted orthonormal semi-internal and singly excited configurations are obtained as

$$\Psi^{a}_{S} = \eta^{*}_{a}\Phi_{S,1/2} + \overline{\eta}^{*}_{a}\Phi_{S,-1/2}\,.$$
(12)

As for the pair functions Ψ_{P} represented by the matrices $\mathbf{C}_{P}$ we may define contracted singly external functions

$$\Psi_{S} = \sum_{a} c^{a}_{S}\,\Psi^{a}_{S}\,,$$
(13)

which are represented by the (column) vectors $\mathbf{c}_{S}$. In the following we shall call the Ψ_{S} simply "singles," but it has to be kept in mind that they contain implicitly the semi-internal doubly excited configurations.

Finally, the singly and doubly internally excited configurations Ψ^{kl}_{ijp} are Schmidt orthonormalized on the reference function Ψ_{0}. If not differently stated, in the following Ψ_{0} is considered as member of the set of internal configurations $\{\Psi_{I}\}$. We note that usually the reference configurations $\{\Psi^{ref}_{k}\}$ span a subspace of $\{\Psi_{I}\}$, so that the coefficients a_{k} entering into Eq. (1) via Ψ_{0} are effectively reoptimized in the CI wave function. This may be used to relax them during the iteration. Of course, the internal coupling coefficients, which will be defined in terms of the Φ_{P}, Φ_{S}, and Ψ_{I} in the next section, have then to be recalculated.

For the sake of simplicity in later expressions we have to define three more types of core functions:

$$\Phi^{I}_{jm} = \begin{cases} \eta_{j}\Psi_{I}\,, & m=1/2\,, \\ \overline{\eta}_{j}\Psi_{I}\,, & m=-1/2\,, \end{cases}$$
(14)

$$\Phi_{jSpm} = \begin{cases} \eta_{j}\Phi_{S,1/2}\,, & p=-1\,, & m=1\,, \\ 1/\sqrt{2}(\eta_{j}\Phi_{S,-1/2} - p\overline{\eta}_{j}\Phi_{S,1/2})\,, & p=\pm 1\,, & m=0\,, \\ \overline{\eta}_{j}\Phi_{S,-1/2}\,, & p=-1\,, & m=-1\,, \end{cases}$$
(15)

and Φ^{I}_{ijpm} which is defined as Φ_{ijpm} [cf. Eq. (6)] but with Ψ_{I} instead of Ψ_{0}.

We note that the construction of the function sets $\{\Phi_{P}\}$, $\{\Phi_{S}\}$, and $\{\Psi_{I}\}$ as described above is not unique, since the individual sets may be subject to any unitary transformation without changing the final wave function.

III. THE HAMILTON MATRIX ELEMENTS

Our aim is to solve the Schrödinger equation which in our configuration basis takes the form

$$\langle \Psi^{ab}_{P} | \hat{H} - E | \Psi \rangle = 0\,, \quad \text{for all } P,\, a,\, b\,,$$
(16)

$$\langle \Psi^{a}_{S} | \hat{H} - E | \Psi \rangle = 0\,, \quad \text{for all } S,\, a\,,$$
(17)

$$\langle \Psi_{I} | \hat{H} - E | \Psi \rangle = 0\,, \quad \text{for all } I\,.$$
(18)

$E = \langle \Psi_{0} | \hat{H} | \Psi_{0} \rangle + E_{\text{corr}}$ is here taken to be the total energy, but other choices for E_{corr} may be used in order to obtain CEPA type solutions.[5,11] In the direct CI method the solution of Eqs. (16)–(18) can be obtained by various iteration schemes. The simplest way is to update the coefficients according to first order perturbation theory[11]

$$C^{ab(n+2)}_{P} = C^{ab(n)}_{P} - \langle \Psi^{ab}_{P} | \hat{H} - E | \Psi^{(n)} \rangle / E^{ab}_{P}\,,$$
(19)

with

$$E^{ab}_{P} \cong \langle \Psi^{ab}_{P} | \hat{H} - E | \Psi^{ab}_{P} \rangle / \langle \Psi^{ab}_{P} | \Psi^{ab}_{P} \rangle\,.$$
(20)

Similar equations can be applied for the coefficients of the semi-internal and internal configurations ($c_{0} = 1$). In order to obtain the quantities $\langle \Psi^{ab}_{P} | \hat{H} - E | \Psi \rangle$, $\langle \Psi^{a}_{S} | \hat{H} - E | \Psi \rangle$, and $\langle \Psi_{I} | \hat{H} - E | \Psi \rangle$ in a compact form, we use the generalized internal Coulomb and exchange operators

$$(\mathbf{J}^{kl})_{rs} = (rs | kl)\,, \quad \mathbf{J}^{kl} = \mathbf{J}^{lk}\,,$$
(21a)

$$(\mathbf{K}^{kl})_{rs} = (rk | ls)\,, \quad \mathbf{K}^{kl} = (\mathbf{K}^{lk})^{+}\,,$$
(21b)

where r, s refer to all orbitals and k, l to internal orbitals only. The J and K represent an ordered subset of the two-electron integrals $(rs | tu)$ in MO basis. An efficient algorithm for their evaluation is given in Ref. 14. In contrast to previous treatments[4,11,14(a)] we here label different operators by superscripts and their matrix elements by subscripts. We further define the external exchange operators

$$[\mathbf{K}(\mathbf{C}_{P})]_{rs} = \sum_{ab} C^{ab}_{P}(ra | bs)$$
(22a)

$$= \sum_{\mu\nu} r_{\mu}\, s_{\nu} \sum_{\rho\sigma} \left(\sum_{ab} C^{ab}_{P}\, a_{\rho}\, b_{\sigma} \right)(\mu\rho | \nu\sigma)\,,$$
(22b)

where r, s, a, b are the orbital vectors and $(\mu\rho | \nu\sigma)$ are the two-electron integrals in AO basis. $\mathbf{K}(\mathbf{C}_{P})$ is the only quantity that depends on integrals with four external orbitals. Finally, we need the Fock operator for the frozen core (in MO basis)

$$\mathbf{F} = \mathbf{h} + \sum_{c}(2\mathbf{J}^{cc} - \mathbf{K}^{cc})\,,$$
(23)

where the index c runs over core orbitals only.

Using the definitions in Sec. II it is now straightforward though somewhat lengthy to derive the following matrix elements:

$$\langle \Psi_{I} | \hat{H} | H_{S} \rangle = \sum_{j} \mathbf{j}^{+}\mathbf{F}\,\mathbf{c}_{S}\sigma(S,\,jI) + \sum_{jkl} \mathbf{j}^{+}\mathbf{J}^{kl}\mathbf{c}_{S}\alpha_{lk}(S,\,jI)\,,$$
(24)

$$\langle \Psi_{I} | \hat{H} | \Psi_{P} \rangle = 1/\sqrt{2} \sum_{kl} \text{tr}\,[\mathbf{C}^{+}_{P}(\mathbf{K}^{kl} + p\mathbf{K}^{lk})]\,\sigma(P,\,klI)\,,$$
(25)

$$\langle \Psi^{a}_{S} | \hat{H} | \Psi_{I} \rangle = \left[\sum_{j} \mathbf{F}\,\mathbf{j}\,\sigma(S,\,jI) + \sum_{jkl} \mathbf{J}^{kl}\mathbf{j}\,\alpha_{lk}(S,\,jI) \right]_{a}\,,$$
(26)

$$\langle \Psi^{a}_{S} | \hat{H} | \Psi_{T} \rangle = \left[\mathbf{F}\,\mathbf{c}_{T}\delta_{ST} + \sum_{kl} \mathbf{J}^{kl}\mathbf{c}_{T}\alpha_{lk}(S,\,T) \right.$$
$$\left. - \sum_{kl} \mathbf{K}^{kl}\mathbf{c}_{T}\beta_{lk}(S,\,T) + \mathbf{c}_{T}\gamma(S,\,T) \right]_{a}\,,$$
(27)

$$\langle \Psi_S^a | \hat{H} | \Psi_P \rangle = p\sqrt{2} \left\{ \sum_j [C_P F + K(C_P)] \, \mathbf{j} \, \sigma(P, jS) \right.$$

$$\left. + \sum_{jkl} C_P J^{kl} \, \mathbf{j} \, \alpha_{lk}(P, jS) \right\}_a , \tag{28}$$

$$\langle \Psi_P^{ab} | \hat{H} | \Psi_I \rangle = 1/\sqrt{8} \sum_{kl} (K^{kl} + pK^{lk})_{ab} \, \sigma(P, klI) , \tag{29}$$

$$\langle \Psi_P^{ab} | \hat{H} | \Psi_S \rangle = \left[K(C_P^S) + 1/\sqrt{2} \sum_j (F \, \mathbf{j} \, c_S^+ + p \, c_S \mathbf{j}^+ F) \sigma(P, jS) \right.$$

$$\left. + 1/\sqrt{2} \sum_{jkl} (J^{kl} \mathbf{j} \, c_S^+ + p \, c_S \mathbf{j}^+ J^{kl}) \, \alpha(P, jS) \right]_{ab} , \tag{30}$$

$$\langle \Psi_P^{ab} | \hat{H} | \Psi_Q \rangle = \delta_{PQ} [F C_P + C_P F + K(C_P)]_{ab}$$

$$+ \left[\sum_{kl} (J^{kl} C_Q + p C_Q^+ J^{lk}) \alpha_{lk}(P, Q) - \frac{1}{2} \sum_{kl} (K^{kl} C_Q \right.$$

$$\left. + p C_Q^+ K^{lk}) \beta_{lk}(P, Q) + C_Q \gamma(P, Q) \right]_{ab} , \tag{31}$$

where

$$C_P^S = 1/\sqrt{2} (\mathbf{j} c_S^+ + p c_S \mathbf{j}^+) \sigma(P, jS) . \tag{32}$$

In Eqs. (24)–(32) $\mathbf{j}$ just denotes the jth unit vector in orbital basis, i.e., $F\mathbf{j}$ is the jth column of the matrix F, and $\mathbf{f} c^+$ denotes the dyadic product of the vectors $\mathbf{f}$ and c, i.e., $(\mathbf{f} c^+)_{kl} = f_k c_l$. The factors σ are simply overlap integrals, α_{kl} and β_{kl} are transition density matrix elements, and γ are Hamilton matrix elements between the core functions indicated by the symbols in parenthesis

$$\sigma(S, jI) = \sum_{m=-1/2}^{1/2} \langle \Phi_{Sm} | \Phi_{jm}^I \rangle , \tag{33}$$

$$\sigma(P, jS) = \sum_{m=-s}^{s} \langle \Phi_{Pm} | \Phi_{jSpm} \rangle , \tag{34}$$

$$\sigma(P, klI) = \sum_{m=-s}^{s} \langle \Phi_{Pm} | \Phi_{klpm}^I \rangle , \tag{35}$$

$$\alpha_{kl}(S, jI) = \sum_{m=-1/2}^{1/2} \langle \Phi_{Sm} | \eta_k^+ \eta_l + \overline{\eta}_k^+ \overline{\eta}_l | \Phi_{jm}^I \rangle , \tag{36}$$

$$\alpha_{kl}(S, T) = \sum_{m=-1/2}^{1/2} \langle \Phi_{Sm} | \eta_k^+ \eta_l + \overline{\eta}_k^+ \overline{\eta}_l | \Phi_{Tm} \rangle , \tag{37}$$

$$\alpha_{kl}(S, jI) = \sum_{m=-s}^{s} \langle \Phi_{Pm} | \eta_k^+ \eta_l + \overline{\eta}_k^+ \overline{\eta}_l | \Phi_{jSpm} \rangle , \tag{38}$$

$$\alpha_{kl}(P, Q) = \sum_{m=-s}^{s} \delta_{pq} \langle \Phi_{Pm} | \eta_k^+ \eta_l + \overline{\eta}_k^+ \overline{\eta}_l | \Phi_{Qm} \rangle , \tag{39}$$

$$\beta_{kl}(S, T) = \langle \Phi_{S,1/2} | \eta_k^+ \eta_l | \Phi_{T,1/2} \rangle$$

$$+ \langle \Phi_{S,-1/2} | \overline{\eta}_k^+ \overline{\eta}_l | \Phi_{T,-1/2} \rangle$$

$$+ \langle \Phi_{S,1/2} | \overline{\eta}_k^+ \eta_l | \Phi_{T,-1/2} \rangle$$

$$+ \langle \Phi_{S,-1/2} | \eta_k^+ \overline{\eta}_l | \Phi_{T,1/2} \rangle , \tag{40}$$

$$\beta_{kl}(P, Q) = \langle \Phi_{P,0} | \eta_k^+ \eta_l + pq \, \overline{\eta}_k^+ \overline{\eta}_l | \Phi_{Q,0} \rangle + \frac{(1-p)(1-q)}{2}$$

$$\times \{ \langle \Phi_{P,1} | \eta_k^+ \eta_l | \Phi_{Q,1} \rangle + \langle \Phi_{P,-1} | \overline{\eta}_k^+ \overline{\eta}_l | \Phi_{Q,-1} \rangle \}$$

$$+ \frac{(1-p)}{\sqrt{2}} \{ \langle \Phi_{P,-1} | \eta_k^+ \overline{\eta}_l | \Phi_{Q,0} \rangle$$

$$+ pq \langle \Phi_{P,1} | \overline{\eta}_k^+ \eta_l | \Phi_{Q,0} \rangle \} + \frac{(1-q)}{\sqrt{2}}$$

$$\times \{ \langle \Phi_{P,0} | \overline{\eta}_k^+ \eta_l | \Phi_{Q,-1} \rangle + pq \langle \Phi_{P,0} | \eta_k^+ \overline{\eta}_l | \Phi_{Q,1} \rangle \} , \tag{41}$$

$$\gamma(I, J) = \langle \Psi_I | \hat{H} | \Psi_J \rangle , \tag{42}$$

$$\gamma(S, T) = \sum_{m=-1/2}^{1/2} \langle \Phi_{Sm} | \hat{H} | \Phi_{Tm} \rangle , \tag{43}$$

$$\gamma(P, Q) = \sum_{m=-s}^{s} \delta_{pq} \langle \Phi_{Pm} | \hat{H} | \Phi_{Qm} \rangle . \tag{44}$$

By inspection of Eqs. (28)–(32) it seems on first sight that the exchange operators $K(C_P)$ and $K(C_P^S)$ have to be calculated for each pair in each iteration. However, for calculating $\langle \Psi_P^{ab} | \hat{H} - E | \Psi \rangle$ only the operator

$$K(\tilde{C}_P) , \quad \text{with} \quad \tilde{C}_P = C_P + \sum_S C_P^S \tag{45}$$

is needed, whereas for calculating $\langle \Psi_S^a | \hat{H} - E | \Psi \rangle$ only the elements $[K(C_P)]_{ak}$ appear (k internal!). One easily verifies that these elements can be obtained as follows:

$$[K(C_P)]_{ak} = [K(\tilde{C}_P)]_{ak} - 1/\sqrt{2} \sum_S \sum_l [p J^{lk} c_S + K^{lk} c_S]_a \sigma(P, lS) \tag{46}$$

Hence, only one external exchange operator has to be calculated per pair and iteration.

By adding up the various matrix elements we obtain for the desired quantities in Eqs. (16)–(18)

$$\langle \Psi_P^{ab} | \hat{H} - E | \Psi \rangle = [\tfrac{1}{2} (G_P + p \, G_P^+) - E C_P]_{ab} , \tag{47}$$

$$\langle \Psi_S^a | \hat{H} - E | \Psi \rangle = [g_S - E c_S]_a , \tag{48}$$

$$\langle \Psi_I | \hat{H} - E | \Psi \rangle = g_I - E c_I , \tag{49}$$

where the matrices G_P, the vectors g_S, and the elements g_I are given by

$$G_P = K(\tilde{C}_P) + 1/\sqrt{2} \sum_{kl} K^{kl} \sum_I c_I \sigma(P, klI)$$

$$+ \sum_Q \left[2\delta_{PQ} F + \sum_{kl} J^{kl} \alpha_{lk}(P, Q) - \sum_{kl} K^{kl} \beta_{lk}(P, Q) + 1 \gamma(P, Q) \right] C_Q + \sqrt{2} \sum_S \left[\sum_j F \, \mathbf{j} \, \sigma(P, jS) + \sum_{jkl} J^{kl} \mathbf{j} \, \alpha_{lk}(P, jS) \right] c_S^+ , \tag{50}$$

$$g_S = \sum_j F \, \mathbf{j} \sum_I c_I \sigma(S, jI) + \sum_{jkl} J^{kl} \mathbf{j} \sum_I c_I \alpha_{lk}(S, jI) + \sum_T \left[\delta_{ST} F + \sum_{kl} J^{kl} \tilde{\alpha}_{lk}(S, T) - \sum_{kl} K^{kl} \tilde{\beta}_{lk}(S, T) + 1 \gamma(S, T) \right] c_T$$

$$+ \sqrt{2} \sum_P p \left\{ \sum_j [C_P F \mathbf{j} + K(\tilde{C}_P)] \, \mathbf{j} \, \sigma(P, jS) + \sum_{jkl} C_P J^{kl} \mathbf{j} \alpha_{lk}(P, jS) \right\} , \tag{51}$$

and

$$g_I = \sum_J \gamma(I, J) c_J + \sum_S \left[\sum_j \mathbf{j}^+ F c_S \sigma(S, jI) + \sum_{jkl} \mathbf{j}^+ J^{kl} c_S \alpha_{lk}(S, jI) \right] + 1/\sqrt{8} \sum_P \sum_{kl} \mathrm{tr}[C_P^+ (K^{kl} + pK^{lk})] \sigma(P, klI) . \tag{52}$$

The factors $\bar{\alpha}$ and $\bar{\beta}$ in Eq. (51) are defined as

$$\bar{\alpha}_{kl}(S,\ T) = \alpha_{kl}(S,\ T) - \sum_P \sigma(P,\ kS)\sigma(P,\ lT)\ , \qquad (53)$$

$$\bar{\beta}_{kl}(S,\ T) = \beta_{kl}(S,\ T) + \sum_P p\,\sigma(P,\ kS)\sigma(P,\ lT)\ . \qquad (54)$$

The structure of the matrices G_P and the vectors g_S is very similar to the closed shell case.[11] The matrices G_P can be written in the simple form

$$G_P = K(\bar{C}_P) + \sum_Q F_{PQ}C_Q + \sum_S f_{PS}c_S^+ + \sum_I F_{PI}c_I\ , \qquad (55)$$

where the matrices F_{PQ} and F_{PI} are linear combinations of internal Coulomb and/or exchange operators and the vectors f_{PS} are linear combinations of particular columns of F and the J^{kl}. In order to avoid storing the F_{PQ}, F_{PI}, and f_{PS}, which would require an exceedingly large amount of mass storage, we recalculate these quantities in each iteration. This is usually fast ($\sim N^2$) as compared to the matrix multiplications in Eq. (55) ($\sim N^3$) and the evaluation of the external exchange operators $K(\bar{C}_P)$ ($\sim N^4$). It is to be noted, that the C_P have nonzero elements only in their external part, i.e., $C_P^{rs} = 0$ if $r \leq M$ or $s \leq M$. Therefore, one only needs the external part of the G_P, and the number of operations for each matrix multiplication in Eq. (55) can be reduced from N^3 to $(N-M)^3$. This saves considerable computation time for systems with many electrons. The evaluation of the vectors g_S involves only ($\sim N^2$) operations and is therefore, in most cases, much faster than the computation of the G_P, even though the number of Φ_S is often considerably larger than the number of Φ_P (cf. Sec. V). We note that it is usually advantageous to perform the summation over T in Eq. (51) first.

We further need the energy denominators in Eq. (20)

$$E_P^{ab} = \epsilon_P^a + \epsilon_P^b + [(aa|bb) + p(ab|ab)]/(1 + \delta_{ab}) - E\ , \qquad (56)$$

where

$$\epsilon_P^a = \left[F + \sum_{kl}(J^{kl}\alpha_{lk}(P,\ P) - K^{kl}\beta_{lk}(P,\ P)/2\right]_{aa} + \gamma(P,\ P)/2\ . \qquad (57)$$

The two-electron integrals in Eq. (56) are not available if one avoids a full integral transformation. Therefore, we replace them in analogy to the closed shell case[11] by the approximations

$$(ab|ab) \cong 0 \qquad (58a)$$

$$(aa|bb) \cong [(J^{ii} + J^{ij})_{aa} + (J^{ii} + J^{jj})_{bb}] \qquad (58b)$$

for $P = (ijp)$. If Φ_{Pm} is a linear combination of several Φ_{ijpm} we just use the indices of the function with the largest coefficient. Such approximations may influence the speed of convergence but have no effect on the final solution. The energy denominators $\langle \Psi_S^a | \hat{H} - E | \Psi_S^a \rangle$ can be evaluated exactly by

$$E_S^a = \left[F + \sum_{kl} J^{kl}\alpha_{lk}(S,\ S) - K^{kl}\beta_{lk}(S,\ S)\right]_{aa} + \gamma(S,\ S) - E\ . \qquad (59)$$

From the above matrix elements the correlation en-

ergy, here defined as $E_{corr} = E - E_0$, may be obtained. For the converged solution E_{corr} can be written as a sum of energy contributions $\epsilon_P^{(1)}$, $\epsilon_S^{(1)}$, and $\epsilon_I^{(1)}$ in the simple way

$$E_{corr}^{(1)} = \sum_P \epsilon_P^{(1)} + \sum_S \epsilon_S^{(1)} + \sum_{\substack{I \\ (\neq 0)}} \epsilon_I^{(1)}\ , \qquad (60)$$

where

$$\epsilon_P^{(1)} = \langle \Psi_P | \hat{H} | \Psi_0 \rangle = \sum_{ab} C_P^{ab} \langle \Psi_P^{ab} | \hat{H} | \Psi_0 \rangle\ , \qquad (61)$$

$$\epsilon_S^{(1)} = \langle \Psi_S | \hat{H} | \Psi_0 \rangle = \sum_a c_S^a \langle \Psi_S^a | \hat{H} | \Psi_0 \rangle\ , \qquad (62)$$

$$\epsilon_I^{(1)} = c_I \langle \Psi_I | \hat{H} | \Psi_0 \rangle\ . \qquad (63)$$

However, $E_{corr}^{(1)}$ is correct only to first order in the errors of the expansion coefficients. Therefore, it is more appropriate to use the energy expectation value, which is of second order accuracy and an upper bound to the true energy in each iteration. It can also be written in partitioned form as follows:

$$E_{corr}^{(2)} = \sum_P \epsilon_P^{(2)} + \sum_S \epsilon_S^{(2)} + \sum_{\substack{I \\ (\neq 0)}} \epsilon_I^{(2)}\ , \qquad (64)$$

where

$$\epsilon_P^{(2)} = [\epsilon_P^{(1)} + \text{tr}(C_P^+ G_P)]/N\ , \qquad (65)$$

$$\epsilon_S^{(2)} = (\epsilon_S^{(1)} + c_S^+ g_S)/N\ , \qquad (66)$$

$$\epsilon_I^{(2)} = (\epsilon_I^{(1)} + c_I g_I)/N\ , \qquad (67)$$

with

$$N = \langle \Psi | \Psi \rangle = \sum_P \text{tr}(C_P^+ C_P) + \sum_S c_S^+ c_S + \sum_I c_I^2\ . \qquad (68)$$

For the converged solution one has $E_{corr}^{(1)} = E_{corr}^{(2)}$, but it should be noted that the partitionings are different.

Finally, the elements of the first order reduced density matrix take the form

$$D_{ab} = \left(\sum_S c_S c_S^+ + 2 \sum_P C_P C_P^+\right)_{ab}\ , \qquad (69a)$$

$$D_{aj} = \left[\sum_S c_S \sum_I c_I \sigma(S,\ jI) + \sqrt{2} \sum_P C_P \sum_S c_S \sigma(P,\ jS)\right]_a\ , \qquad (69b)$$

$$D_{ij} = \sum_{IJ} c_I c_J \alpha_{ij}(I,\ J) + \sum_{ST} c_S^+ c_T \alpha_{ij}(S,\ T) + \sum_{PQ} \text{tr}(C_P^+ C_Q)\alpha_{ij}(P,\ Q)\ . \qquad (69c)$$

IV. COMPUTATIONAL ASPECTS

In our program, first the operators F, J^{kl}, and K^{kl} are evaluated and transformed into MO basis. This corresponds to a partial integral transformation which requires about $\frac{3}{8}N^4M + 3N^3M^2 + \frac{11}{8}N^3M$ operations,[14] where N is the number of basis functions and M is the number of correlated orbitals. Since usually $M \ll N$ the time required for this step is very small as compared to a full integral transformation.

In the second program step, the internal factors σ, α, β, and γ are calculated. In principle, this can be done by any of the well-known CI techniques. However, due to the relatively complicated structure of the core

functions Φ_P, Φ_S, and Ψ_I, many of these techniques, which often rest upon specific spin couplings, cannot straightforwardly be applied. In our present program, the core functions are therefore represented in determinantal form and the factors are calculated in a rather brute force way according to Eqs. (33)–(44), (53), and (54). For the systems studied so far, the time needed for this step was always small as compared to the total time.

The iteration process proceeds in the following sequence: first, the internal coefficients c_I are determined. This is a very fast process which can be done exactly for fixed c_S, C_P in each iteration. Secondly, the operators $K(\tilde{C}_P)$ are evaluated. Often, all $\tilde{C}_P$ and $K(\tilde{C}_P)$ can be stored simultaneously in high speed memory, so that all operators can be evaluated efficiently during one sequential read of the integral file. Thirdly, the matrices G_P and the vectors g_S are computed and improved C_P and c_S are obtained. During the individual steps the various contributions to the energy expectation value are summed up. At the end of the iteration this yields the energy which corresponds to the c_I of the present and the C_P, c_S of the preceding iteration.

The efficiency of any direct CI approach depends, of course, on the number of iterations required. In order to speed up and guarantee convergence (in the sense that $E^{(n+1)} \leq E^{(n)}$) various improved iteration schemes, as for instance the well known Davidson technique,[41] can be devised. The improvement of convergence by using Davidson's method is, however, not very large, which is mainly due to the small number of variational parameters. A more effective "scaling procedure," which also guarantees convergence, is briefly outlined in the following. The wave function is expanded as

$$\Psi^{(n+1)} = \Psi^{(n)} + \sum_P \lambda_P \Delta\Psi_P^{(n)} + \sum_S \lambda_S \Delta\Psi_S^{(n)} + \sum_I c_I \Psi_I . \tag{70}$$

The parameters c_I, λ_S, and λ_P can be determined variationally by performing a small CI in the basis of the functions $\Psi^{(n)}$, Ψ_I, $\Delta\Psi_S$, and $\Delta\Psi_P$. The Hamilton matrix elements needed are easily evaluated during the calculation of $\Delta G_P^{(n)}$ and $\Delta g_S^{(n)}$. For instance,

$$\langle \Delta\Psi_P^{(n)} | \hat{H} | \Psi^{(n)} \rangle = \text{tr}(\Delta C_P^{+(n)} G_P^{(n)}) , \tag{71}$$

$$\langle \Delta\Psi_P^{(n)} | \hat{H} | \Delta\Psi_Q^{(n)} \rangle = \text{tr}(\Delta C_P^{+(n)} F_{PQ} \Delta C_Q^{(n)})$$
$$+ \delta_{PQ} \, \text{tr}[\Delta C_P^{+(n)} K(\Delta C_P^{(n)})] , \tag{72}$$

$$\langle \Delta\Psi_P^{(n)} | \hat{H} | \Delta\Psi_S^{(n)} \rangle = \Delta c_S^{+(n)} \Delta C_P^{+(n)} f_{PS}$$
$$+ \sqrt{2} \sum_j f^+ K(\Delta C_P^{(n)}) \Delta c_S^{(n)} \sigma(P, jS) , \tag{73}$$

etc. Using the optimal parameters λ_P the improved coefficients are obtained as

$$C_P^{(n+1)} = C_P^{(n)} + \lambda_P \Delta C_P^{(n)} , \tag{74}$$

and similarly for $c_S^{(n+1)}$. For the first iteration (i.e., with $\Psi^{(1)} = \Psi_0$) the above scheme corresponds to the externally contracted CI method proposed by Siegbahn.[25,36] However, since in the latter treatment the configurations are generated from the individual reference configurations the number of parameters λ is usually larger than in our case. Unfortunately, the above scheme re-

quires calculating the operators $K(\Delta C_P)$, whereas for ΔG_P $K(\Delta\tilde{C}_P)$ is needed. If the operators are calculated directly from the two-electron integrals in AO basis this increases the computational effort for the N^4 step by a factor of 2. Therefore, on the one hand, the advantage of using the scaling procedure depends on the number of iterations saved; on the other hand, it will probably be most useful for calculations with many pairs and relatively small basis sets, since then the evaluation of the $\sum_Q F_{PQ} C_Q$ becomes more expensive than the computation of the $K(\tilde{C}_P)$. However, several variants of the scaling procedure are possible, which have to be tested in practice. For instance, one may apply it only to the pair functions in intermediate iterations, for which the c_S and $K(C_P^S)$ are kept fixed. Presently, we have implemented only a simpler scaling procedure, where the scaling factors are determined individually by minimizing the energy for

$$\Psi = \Psi_0 + \lambda_P \Psi_P . \tag{75}$$

This simple procedure, which completely neglects the coupling of the pairs, does not guarantee but often stabilizes convergence.

In order to save computation time it is sometimes advantageous not to calculate all G_P, g_S in each iteration. In our program it is therefore possible to improve the c_S for fixed C_P, c_I, or the C_P for fixed c_S, c_I several times. In certain cases some C_P converge considerably faster than the majority, e.g., if core–core or core–valence correlation effects are considered. Then considerable computation time can be saved by freezing such C_P for several intermediate iterations. On the other hand, it is sometimes advantageous to perform additional iterations only for those pairs which converge most slowly.

The speed of convergence can also be influenced by the choice of the external orbitals, which may be subject to any unitary transformation without influencing the final energy. In the original SCEP formalism[11] Meyer proposed to determine "optimal" correlation orbitals for each pair by diagonalizing the external part (i.e., $O_{ir} = O_{ri} = 0$ for $i \leq M$) of the operator

$$O_P = F_{PP} + \tfrac{1}{2}(J^{ii} + J^{jj}) , \tag{76}$$

$[P = (ijp)]$. In each iteration one has then to transform G_p to the basis of the eigenfunctions of O_p. The ΔC_p are now determined in the new basis and finally transformed back to the original one. According to our experience with the closed-shell SCEP program such transformations are often not necessary if canonical Hartree–Fock orbitals are employed as a common set. However, if one uses a localized internal orbital set— e.g., because many pairs are then negligible in larger molecules—the delocalized external orbitals may lead to poor convergence. In such cases, the optimal correlation orbitals often considerably speed up convergence. Another reason for the use of improved correlation orbitals may be that the MCSCF process yields completely arbitrary external orbitals. Possibly, it will be sufficient in most cases to use a common set of orbitals for all pairs by diagonalizing one suitably chosen operator.

TABLE I. Calculated energies for the $^3B_1$ and $^1A_1$ states of CH_2.[a]

Method	Reference	Basis	$^3B_1$		$^1A_1$		ΔE_{ref}	ΔE_{CI}
			E_{ref}	E_{tot}	E_{ref}	E_{tot}		
CMR—CI	This work	(642/42)[b]	−38.9327	−39.0630	−38.9148	−39.0461	11.2	10.6
MR—PNO—CI	8	(642/42)	−38.9330	−39.0596	−38.9154	−39.0427	11.1	10.6
MR—CI	43	(642/32)	−38.9333	−39.0622	−38.9157	−39.0453	11.1	10.6
MR—CI	44	(853/41)	−38.9336	−39.0695[c]		−39.0527[c]		10.5
MRD—CI	45	(542/21)[d]	−38.9307	−39.0614				12.1/11.1[e]
GVB—POL—CI	46	(532/21)						10.6/10.4[f]
MCSCF	47	(963/42)	−38.9348		−38.9175		10.9	
CMR—CI	This work	(9621/52)[g]	−38.9341	−39.0715	−38.9170	−39.0562	10.7	9.6
CMR—CI	This work	(9721/52)[h]	−38.9341	−39.1160[h]	−38.9170	−39.1003[h]	10.7	9.8/9.3[f]
Experiment	49(a)							~9.0
	49(b)							19.5

[a]E in a.u., ΔE in kcal/mol.

[b]GTO basis set of Huzinaga (Ref. 50); C: $11s/6p$ (521111/3111); d: 1.3, 0.4; H: $6s$ (3111); p: 1.0, 0.25; geometry as in Ref. 8: $^3B_1$: $\alpha = 132.3°$, $r = 2.04$ a.u.; $^1A_1$: $\alpha = 101.4°$, $r = 2.101$ a.u. .

[c]All singles and doubles with respect to full valence reference state functions.

[d]With additional basis functions in the middle of the bonds.

[e]Variational and extrapolated results.

[f]T_e and T_0, respectively.

[g]GTO basis set of Huzinaga (Ref. 50); C: $11s/7p$ (311111111/211111); d: 1.3, 0.4; f: 0.65, H: $7s$(31111); p: 1.0, 0.25; at the optimized geometries: $^3B_1$: $\alpha = 132.9°$, $r = 2.037$ a.u.; $^1A_1$: $\alpha = 102.0°$, $r = 2.095$ a.u. .

[h]With core—core and core—valence correlation; basis as footnote g but p functions not contracted.

Finally, we note that sometimes considerable computation time can be saved by defining equivalent pairs according to molecular symmetry.[11,42] In such cases one needs to calculate the G_P, $K(\tilde{C}_P)$ only for one of the equivalent pairs. The C_P for the remaining pairs can be generated by simple symmetry considerations. For instance, in CH_4 one can localize the internal orbitals so that four equivalent bond orbitals are obtained. The number of different G_P to be calculated is then reduced from 16 to three (valence shell correlation only).

V. APPLICATIONS

The purpose of this section is twofold: first, we wish to demonstrate the efficiency of our method for some examples and compare it with other calculations recently reported in the literature. Secondly, we have calculated the potential and dipole moment functions for the two lowest states of the OH radical in order to compare the accuracy of the CMR—SCEP results with previous accurate uncontracted MR—CI and PNO—CEPA calculations.

The comparison of computation times for various methods on the basis of particular programs running on different machines can, of course, give only a rough indication about the relative efficiency. The times depend on the specific installation and conversion factors may be different for individual program steps. All CPU times quoted in this paper refer to a DEC KL/1091 computer with double precision arithmetic for all floating point operations. For comparison we note that we found the DEC-10 machine to be about 20% slower than a UNIVAC 1108 and five times slower than a IBM 370/168.

Unfortunately, in the literature often the CPU times for CI calculations are given without the time needed for the preceding integral transformation. Clearly, the total times (including integral sorting or symmetry orbital transformation steps) should be compared with the times given below for the SCEP program.

As a first example we chose the CH_2 radical, since Taylor[8] recently presented complete computation times for MR—PNO—CI calculations for this system. He calculated the $^3B_1$ state with a one determinant RHF reference function and the $^1A_1$ state with a two-configuration reference function. Similar MR—CI calculations have been reported previously by Bauschlicher and Shavitt (BS).[43] Following Taylor, we first used a (642/42) contracted GTO basis set. In Table I our calculated energies are compared to the results of various other MR—CI calculations. The singlet—triplet splitting is virtually the same as obtained by Taylor and BS with similar basis sets. For comparison we have also calculated the energies with a considerably larger (9621/52) basis set. With this basis the computed reference energies are close to the best previous values of Meadows and Schaefer,[47] and the variational total energies for the correlated wave functions are lower than in any other previous CI calculation. With respect to the smaller basis the calculated $S-T$ splitting is reduced by about 1 kcal/mol. This lowering is mainly due to the inclusion of the f function into the carbon basis set, which has not been done in any other of the former calculations. Including the core—core and core—valence correlation effects and taking into account the difference of the zero point energies of about -0.55 kcal/mol[48] we obtain a singlet—triplet splitting of 9.3 kcal/mol, which is in good agreement with the value of about 9 kcal/mol obtained from (indirect) photochemical experiments.[49(a)] However, there is a large discrepancy with the value of 19.5 kcal/mol obtained from (direct) photodetachment experiments.[49(b)] It has been proposed[45,46] that this difference can be removed by assigning some peaks in the photoelectron spectrum of CH_2^- to "hot

TABLE II. Details of the CH_2 calculations.

State	$^3B_1$	$^1A_1$	$^1A_1$
Basis	(642/42)	(642/42)	(9621/52)
Number of orbitals	48	48	66
Number of configurations[a]	3454	3359	6980
Computation times in seconds[b] per iteration step			
Internal factors	2.5	2.7	2.7
Operators F, J^{kl}, K^{kl}	39.5	41.2	123.9
Operators $K(C_p)$	45.5	49.0	151.7
$\Sigma_Q F_{PQ} C_Q$, ΔC_P	17.9	18.8	46.7
Singles, internals	5.7	5.0	8.7
Density matrix	2.8	2.8	5.9
Fixed time	48.5	52.5	135.8
Time per iteration	70.5	73.9	207.1
Total time (five interations, energy converged to 10^{-6} a.u.)	401	422	1171
MR–PNO–CI, Ref. 8[c]	3409	5402	

[a] $^3B_1$: one reference configuration, 13 pairs, 20 singles, two internals; $^1A_1$: two reference configurations, 13 pairs, 18 singles, five internals.
[b] DEC KL/1091 double precision ($\sim 20\%$ slower than UNIVAC 1108 and five times slower than IBM 370/168).
[c] On UNIVAC 1108.

bands, " but this assignment could not be confirmed by new experiments of Lineberger et al.[51] We note that preliminary CI calculations with very large and flexible basis sets indicate that the experimental electron affinity of 0.21 eV[49(b)] for the $^3B_1$ state, which is consistent with the $S-T$ splitting of 19.5 kcal/mol, is much too low. A value of 0.67 eV, which corresponds to an $S-T$ splitting of 9 kcal/mol, seems to be more likely.

The computation times for the various steps of the SCEP calculations for CH_2 are listed in Table II. The time needed for the internal factors is negligible. The calculation of the internal Coulomb and exchange operators J^{kl} and K^{kl} requires about 10% of the total time. About 90% of the iteration time is spent for the calculation of the external exchange operators $K(C_P)$ and for the pair contributions to G_P. Here we should like to emphasize that the computation of the $K(C_P)$ should not

be considered a price one has to pay for circumventing the full integral transformation. Instead, this step is in a completely equivalent way part of evaluating Hc in any direct CI method. Thus the effort for a full integral transformation should be compared only with the evaluation of the internal operators J^{kl} and K^{kl} and the four matrix multiplications per pair per iteration contained in Eq. (22b). The semi-internal and internal configurations require only very little time. Hence, a "first order CI calculation," which includes only these configurations, would be extremely fast, since no matrix multiplications and no external exchange operators are required. The total computation time for each state in order to obtain the correlation energy with an accuracy of 10^{-6} a.u. amounts to about 7 min (five iterations). The times for the large basis set are about three times larger. The convergence of the CI iteration process is demonstrated in Table III. Only three iterations (4.5

TABLE III. Convergence of the CI calculations for CH_3.[a]

Iteration	$E_{CI}-E_{Ref}$			
	$^3B_1$	$^1A_1$	ΔE (kcal mol^{-1})	CPU time (min)
0[b]	-0.115276	-0.122900	12.8	0.9
1[c]	-0.108033	-0.171233	11.8	2.1
2	-0.129929	-0.130557	10.9	3.3
3	-0.130304	-0.131194	10.6	4.6
4	-0.130325	-0.131252	10.6	5.8
5	-0.130326	-0.131260	10.6	7.0

[a] Basis (642/42), see Table I.
[b] Perturbational energies.
[c] Variational energies corresponding to the wave function of the preceding iteration.

TABLE IV. Results of barrier height calculations for the $CH_2\,(^3B_1)+H_2$ abstraction reaction.[a]

Method	Reference	Basis[b]	Reactants	Saddle point	Barrier height
SCF	this work	A	−40.052 093	−40.015 228	23.2
MCSCF(5)[d]	this work	A	−40.070 322	−40.043 933	16.6
MCSCF(9)[c]	this work	A	−40.070 322	−40.044 175	16.4
MCSCF(9)[c]	25(b)	A'			17.8
CMR(5)−CI	this work	A	−40.199 294	−40.184 000	9.6
MR(5)−CI	26(b)	A'			11.3
SD−CI	53	DZ P[e]	−40.203 98	−40.182 23	13.65[f]
					11.8[g]
SCF	this work	B	−40.065 173	−40.026 469	24.3
MCSCF(5)[d]	This work	B	−40.083 696	−40.055 362	17.8
CMR(5)−CI	This work	B	−40.232 110	−40.215 031	10.7

[a]Geometries see Ref. (53).
[b]Basis A: Dunning [54]DZ contraction of Huzinaga's (Ref. 50) $9s/5p$ set; d_C: 0.7, p_H: 0.7.
A': as basis A but without p functions on the H atoms of CH_2. B: basis (642/42), see Table I.
[c]All configurations which can be formed from the $3a_1$, $4a_1$, $5a_1$, and $1b_1$ orbitals with doubly occupied $1a_1$, $2a_1$, and $1b_2$ orbitals.
[d]The five configurations with largest coefficients in a natural orbital description of MCSCF(9).
[e]As basis A, but exponents of polarization functions d_C: = 0.74, p_H: 1.0.
[f]Variational result.
[g]With Davidson's (Ref. 52) correction.

min CPU time) for each state are required in order to obtain the $S-T$ splitting with an accuracy of three decimal figures.

In the CH_2 system the number of pairs and singles is quite small. As a larger example we have performed some calculations for the $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$ reaction barrier. This system was chosen in order to compare with calculations reported by Siegbahn[25] using a GUGA direct-CI method. The geometries for the transition state and the reactants were taken from the work of Bauschlicher.[53] The results are presented in Table IV. As for CH_2 we have employed two basis sets: a small one (A in Table IV) which is of double zeta plus polarization quality and essentially the same as used by Siegbahn.[25] The only difference to Siegbahn's basis set (A') is that we did not omit the polarization functions at the hydrogen atoms of CH_2. The larger basis set (denoted B) is the same (642/42) contracted set used for the CH_2 calculations (cf. Table I). By comparison of the data for basis A and A' it is found that the additional polarization functions lead to a considerable lowering of the calculated barrier height already at the Hartree−Fock and MCSCF levels. However, enlarging the basis set then increases the calculated barrier height by about 1 kcal/mol. The final CI value of 10.7 kcal/mol is not considered to be very reliable, since we neither optimized the geometries nor investigated the effect of further basis set improvements. The calculations are simply examples chosen to give an idea of the computational effort needed and how that effort increases if the basis is enlarged by approximately a factor of 2 (this is the case for each symmetry block). Some details and the timings are given in Table V. For the small basis set the evaluation of the $K(\tilde{C}_P)$ ($\sim N^4$) the pair contributions $\Sigma_Q F_{PQ}C_Q$ to G_P ($\sim N^3$) and the remaining effort for the internal and semi-internal configurations ($\sim N^2$) take approximately the same time. For the twice as large basis set the times for the three steps increase

by factors of 10.7, 7.4, and 2.4, respectively, which quite nicely demonstrates the expected basis set dependence.

TABLE V. Details of the $CH_2(^3B_1) + H_2$ calculations.[a]

Basis	(421/21)	(642/42)
Number of orbitals	35	68
Number of configurations[b]	4378	18703

Computation times in minutes per iteration[c]

Step

Internal factors	2.6	2.6
Operators F, J^{kl}, K^{kl}	0.48	4.4
Operators $K(C_P)$	0.70	7.5
$\Sigma_Q F_{PQ} C_Q$, ΔC_P	0.65	4.8
Singles, internals	0.70	1.7
Density matrix	0.13	0.4
Fixed time	3.2	7.6
Time per iteration	2.0	14.0
Total time (six iterations, Energy converged to 10^{-6} a.u.)	15.5	92.0

Times for other direct CI[d] [Ref. 25(b), five reference configurations, 30 orbitals, 16 096 configurations]

Fixed time	1.9 + integral transfer
Time per iteration	26.4

[a]At the reaction barrier, geometry see Ref. (53).
[b]Five reference configurations, 32 pairs, 98 singles, 26 internals.
[c]On DEC KL/1091, see Table II.
[d]On CDC 6400. This computer is about as fast as the DEC-10.

TABLE VI. Calculated molecular constants for OH $(X\,^2\Pi)$. [a]

Method	Reference	r_e	B_e	α_e	ω_e	$\omega_e x_e$	D_e	μ_e	$(d\mu/dr)_{r_e}$
RHF	This work	0.950	19.69	0.658	4056.6	75.5	2.99	1.765	0.82
MCSCF(3)	This work	0.973	18.78	0.788	3666.7	97.8	3.63	1.676	0.25
RHF–CI	This work	0.967	19.02	0.694	3819.0	81.2		1.693	0.57
CMR(3)-CI	This work	0.971	18.84	0.728	3737.4	88.2	4.39	1.672	0.405
Experiment	60	0.970	18.91	0.724	3737.8	84.9	4.63	1.668	
PNO–CI	5(c)	0.966	19.06	0.695	3841	80.2	4.22	1.705	0.55
PNO–CEPA	5(c)	0.971	18.85	0.727	3742	85.3	4.35	1.683	0.40
MR(3)-CI	55	0.794	18.87	0.68	3713.0	83.2	4.43	1.634	0.40
MCSCF	58	0.972	18.79	0.628	3723.6	83.2	4.70	1.675	0.59

[a] D_e in eV, μ_e in D, $(d\mu/dr)_{r_e}$ in D/Å, r_e in Å, all other values in cm^{-1}. Basis set (52 contractions): O: 11s/6p GTO basis set of Huzinaga (Ref. 50), innermost 3s and 2p contracted; d: 2.626, 0.657; f: 1.313; H: 6s set of Huzinaga, innermost 3s contracted. p: 1.2, 0.3; d_σ: 0.75.

dency. The timings for the small basis set calculations can be compared to those given by Siegbahn for the same system. In this context it is important to note that the number of configurations included in Siegbahn's uncontracted MR–CI calculations is much larger (16 096 for 30 basis functions) than in our CMR–CI calculations (4378 for 35 basis functions). Clearly, this makes the former calculations much more expensive. Even our calculations with the more than twice as large basis set (18 703 configurations for 68 basis functions) is considerably faster. Of course it is not clear whether the time difference is only due to the different number of configurations and pairs. In any case, the restriction to small basis sets which may be required for the expensive uncontracted MR–CI calculations seems to intorduce much larger errors than generating the configurations from a contracted reference function.

Finally, we present calculations for the ground state $(X\,^2\Pi)$ and the first excited state $(A\,^2\Sigma^+)$ of OH. This system has been chosen in order to compare the CMR–SCEP results to previous MR–CI calculations of Chu, Yoshimine, and Liu (CYL)[55] and PNO–CI, and PNO–CEPA calculations of Meyer.[5(c),56] As CYL we employed for the ground state just the three reference configurations which are needed to properly describe the dissociation of the molecule into the O (^3P) + H state; for the excited state the same five reference configurations as chosen by CYL have been used, although only two of

them are needed to describe the asymptotic O (^1D) + H state. For comparison with the PNO–CI results of Meyer, we have performed also single-reference-CI (RHF–CI) calculations for the ground state around the equilibrium distance. The (9521/421) contracted GTO basis set is essentially the same as used in Ref. 5(c). The calculated spectroscopic constants are compared to experimental and the previous theoretical data in Tables VI and VII. As expected, the RHF–CI results are in good agreement with the corresponding PNO–CI values. Moreover, the CMR–CI results for the ground state are in excellent agreement with the experimental data and the PNO–CEPA values. The MR–CI results of CYL for the $^2\Pi$ state are somewhat less accurate, which is probably due to basis set deficiencies. It is to be noted, that the MR–CI results are considerably more accurate than the RHF–CI values. This is accomplished with only a doubling of the computation times (RHF–CI: 15 pairs, 16 singles, 14 min CPU time; CMR–CI: 22 pairs, 53 singles, 10 internals, 25 min CPU time for energy converged to 10^{-6} a.u.; only C_{2v} symmetry used). Of course, near the equilibrium distance SCEP–CEPA calculations could be performed with the same effort as required for the RHF–CI calculations, but the one-reference determinant approximation breaks down at larger distances.

For the $A\,^2\Sigma^+$ state (Table VII) the results are somewhat less accurate. Again our CMR–CI data are in

TABLE VII. Calculated molecular constants for OH $(A\,^2\Sigma^+)$. [a]

Method	Reference	r_e	B_e	α_e	ω_e	$\omega_e x_e$	D_e	T_e	T_∞
RHF	This work	0.997	17.86	0.895	3322[b]	115.6	0.91	4.28	
MCSCF(5)	This work	0.997	17.88	0.924	3322[b]	129.0	1.11	4.72	2.19
CMR(5)-CI	This work	1.008	17.50	0.865	3242[b]	100.9	2.23	4.19	2.04
					3245[c]	102.3			
Experiment	60	1.012	17.36	0.787	3178.9	92.9	2.49	4.05	1.97
PNO–CEPA	5(b)	1.009	17.46	0.819	3248	96.9	2.23	4.15	
MR(5)-CI	55	1.008	17.50	0.88	3198.5[c]	106.2	2.29	4.17	2.03

[a] r_e in Å, D_e, T_e, and T_∞ in eV, other values in cm^{-1}. Basis set see Table VI.
[b] From polynomial fit of seventh degree.
[c] From first two ΔG values.
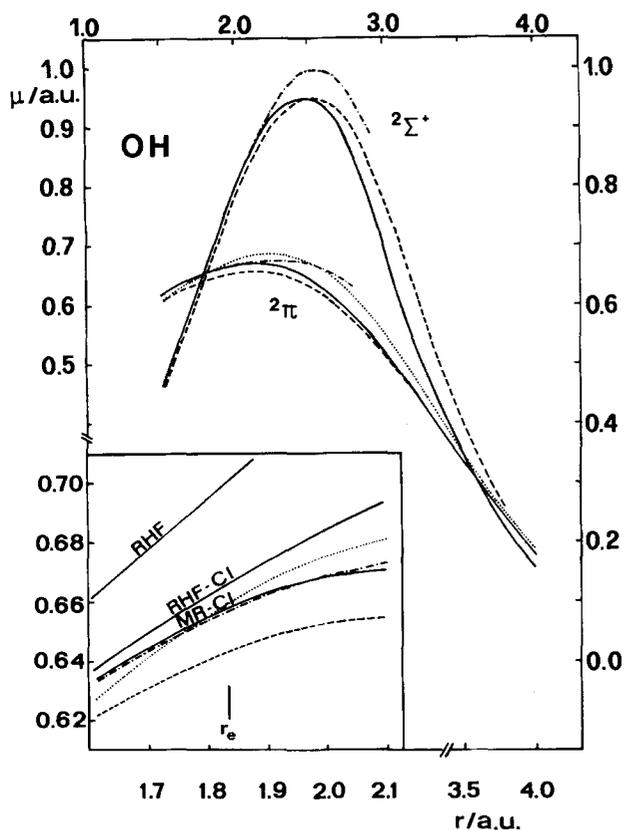
FIG. 1. Calculated dipole moment functions (in a. u.) of the OH radical. —: MR–CI, this work; – – –: MR–CI, Ref. 55; –·–: PNO–CEPA, Refs. 5(c) and 56; ···: MCSCF(17), Ref. 58. The small figure in the lower part shows the EDMF's for the $^2\Pi$ state on a larger scale. The calculated energies and dipole moments for 15 internuclear distances between 1.5 and 10 bohr are available on request.

very good agreement with the PNO–CEPA values of Meyer, but in both cases the equilibrium distance is about 0.004 Å too short and, as a consequence, ω_e is about 60 cm^{-1} too large. These errors are probably due to basis set defects. In view of the fact that the equilibrium distance obtained by CYL displays the same error, their considerably better ω_e value seems to be fortuitous.

The calculated dipole moment functions (EDMF's) for the two states are shown in Fig. 1. To our knowledge, no accurate function for OH has been determined experimentally. It is well known, that the RHF and RHF–CI approximations do not produce reliable EDMF's, whereas the CEPA method has been shown to yield very accurate EDMF's around the equilibrium distances of molecules with single bonds.[16,56,57] In fact, our CMR–SCEP functions are in perfect agreement with Meyer's CEPA functions up to a distance of about 2.1 Bohr. At larger distances, in particular beyond the maxima of the EDMF's the MCSCF function falls off too rapidly, and the differences between the MCSCF and CEPA dipole moments become very large. It seems that either CEPA-like corrections or better reference wave functions are required in order to fully account for this large correlation effect. Near the equilibrium distances the

dipole moment functions of CYL also closely parallel the CMR–SCEP curves, but are shifted to lower values. For the ground state we have tried various extensions of the basis set at the equilibrium distance, which did not lead to a significant change of the dipole moment. Therefore, the shifts of CYL's functions seem to be due to basis set defects. Finally, we note that the dipole moment function of Stevens et al.[58] obtained from MCSCF wave functions near the equilibrium distance probably has a slope that is much too large. Unfortunately, this function has been used by Mies[59] to determine infrared transition probabilities, which are now widely used by experimentalists. According to the error of $(d\mu/dr)_{r_e}$ it is to be expected that the Einstein coefficient of spontaneous emission for the fundamental transition obtained by Mies are considerably too large.

VI. SUMMARY

An iterative CI method has been described which is able to produce highly accurate results at a moderate expense. The wave functions optimized consist of all singly and doubly excited configurations which can be generated from a contracted multiconfiguration (MCSCF) reference function (CMR–CI). According to our preliminary experience with wave functions of this type virtually the same results are obtained as with more general MR–CI treatments, which include all singles and doubles with respect to the individual reference configurations. However, near avoided crossings, where two internal states are nearly degenerate, it may be important to relax the internal contraction coefficients. Judging by the examples given in this contribution, it seems that the computation times for the CMR–SCEP method are one order of magnitude less than reported for other MR–CI programs, even for quite simple systems with only a few reference configurations. On the one hand, this improvement results from the reduction of the number of pairs, which for a given basis set mainly determines the computational effort for any direct CI method. But on the other hand, part of the improvement may be due to the fact that the SCEP method is based on simple matrix operations, which can be efficiently performed with very little index operations. Since only very few matrices have to be kept simultaneously in high speed memory and a full transformation of the two-electron integrals is avoided, very large basis sets can be used even on relatively small computers without making the calculation exceedingly expensive. Furthermore, as has been discussed in Sec. IV, the matrix structure enables a great flexibility of the method. Finally, we note that during the preparation of this paper it came to our knowledge that Ahlrichs[61] has simultaneously developed an MR–CI formalism which is closely related to our treatment.

Note added in proof. In order to compare directly the results obtained with contracted and uncontracted MR–CI wave functions, we have performed some additional uncontracted MR–SCEP calculations. For the CH_3 ($^3B_1$) + H_2 system, one obtains (saddle point, basis A): 104 pairs, 186 singles, 27 internals, 12 974 configurations, $E_{MR-CI} = -40.184319$, i.e., the correlation energy is lowered by only 0.2%. This negligible im-

provement is payed for by a factor of more than three in the computation time (CPU time per iteration: 6.4 min). For the ground state of OH, the uncontracted MR–SCEP results are (in cm^{-1}): $B_e = 18.83$, $\alpha_e = 0.726$, $\omega_e = 3736.1$, $\omega_e x_e = 87.2$. The correlation energy at the equilibrium distance is improved by only 0.14%. Between $r = 1.5$ bohr and $r = 2.5$ bohr, the dipole moment functions differ by less than 0.004 D. The largest deviation occurs at about 3.5 bohr and amounts to 0.02 D.

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