The Direct Configuration Interaction Method from Molecular Integrals

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1. Introduction

In this paper we will address ourselves to some aspects of the problem of finding accurate solutions to the electronic Schrödinger equation by means of the configuration interaction (CI) method. This method is probably one of the most encouraging for general studies of molecular systems in their ground and excited states, and also for studies of energy surfaces for chemical reactions.

The general scheme for configuration interaction calculations was first proposed by Boys in 1950,[1] who also carried through a ten-configuration calculation on the beryllium atom.[2] Methods similar in philosophy to the CI method had earlier been used by Hartree, Hartree, and Swirles in their study of the oxygen atom[3] and by Hylleraas for the helium atom.[4] The numerical difficulties, however, prohibited further developments of the theory until the electronic computer came into general use and the problem of integral evaluation and the handling of large amounts of numerical data could be efficiently dealt with.

A number of computer programs for *ab initio* calculations on molecular systems on the Hartree–Fock level of approximation were constructed in the

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period 1965–1970 and such calculations are routinely performed today in many laboratories. This development has been of great importance for the application of *ab initio* quantum mechanical methods in studies of a variety of current problems in molecular chemistry and physics, since the Hartree–Fock method is known to yield reliable results for many chemical processes. The Hartree–Fock method can, however, only be used for processes in which the correlation error can be assumed not to vary. Many problems do not belong to this category and it is necessary to include correlation effects in these cases in order to be able to make useful predictions. The most commonly used method for treating these effects is the method of configuration interaction. Today's research in computational quantum chemistry is therefore, to a large extent, centered around the problem of finding efficient tools to use this method in practice.

It is customary to differentiate between two types of correlation effects. The Hartree–Fock model will in certain cases break down due to degeneracies or near degeneracies between several configurations. Such effects frequently occur in calculations of energy surfaces for chemical reactions. They can be dealt with by means of a limited CI expansion which includes all near-degenerate configurations. An extension of the Hartree–Fock method to cases with more than one configuration is then obtained, when the CI expansion coefficients and the orbitals are simultaneously optimized. This procedure constitutes the MC–SCF (multiconfigurational self-consistent-field) method.[3,5-7]

The second effect is the dynamic correlation of the electronic motion. For electrons with parallel spins, this correlation is already to a large extent included in the Hartree–Fock model, through the antisymmetry requirement (Fermi correlation). The main part of the remaining error is, therefore, due to correlation of electron pairs having opposite spins. The fact that electron correlation to a good approximation is described by pair interactions, implies that the dominant part of the correlation energy is obtained with a CI wave function which contains replacements in each pair of electrons. For special reasons single replacements are also important and the wave function describing dynamical correlation effects should, in general, contain the near-degenerate configurations and single and double replacements with respect to all of them.

Such an expansion will in general be very long, since the number of possible double-replacement configurations is large for a reasonably sized molecule orbital basis set. One of the obstacles in using the CI method is therefore the problem of calculating and handling a very large number of matrix elements. In special cases it is possible, however, to avoid the construction of a huge Hamiltonian matrix and instead calculate the CI expansion coefficients directly from the given list of molecular one- and two-electron integrals. This is the philosophy behind the CIMI method[8,9] (direct *configura-*

tion *interaction* from *molecular integrals*) which will be discussed in detail in the following sections. Computer programs for CI calculations using different versions of the CIMI method have been included in the general quantum chemistry program system MOLECULE.[10]

2. The CIMI Method

2.1. General Scheme

In this section general concepts of the configuration interaction scheme are presented in their context, and the basic characteristics of the CIMI method as compared to other methods are described.

The wave function is in the CI method expressed as a linear combination of configuration *state functions* (CSFs), i.e.,

$$\Psi = \sum_\mu C_\mu \Phi_\mu \tag{1}$$

where the CSFs are linear combinations of Slater determinants having correct spin and space symmetry.

The expansion coefficients C_μ are obtained by applying the Rayleigh–Ritz variation principle

$$\sum_\nu (H_{\mu\nu} - ES_{\mu\nu})C_\nu = 0 \tag{2}$$

with

$$H_{\mu\nu} = \langle \Phi_\mu | \hat{H} | \Phi_\nu \rangle$$

$$S_{\mu\nu} = \langle \Phi_\mu | \Phi_\nu \rangle$$

The eigenvalues obtained from (2) are upper bounds to the true eigenvalues of the Hamiltonian.[11] The actual solution of the equation system (2) is, in practice, divided into several parts, which will be briefly described here.

The Slater determinants, which are used to construct the CSFs, are built from an ordered set of one-electron functions (orbitals). These orbitals are in turn usually obtained as linear combinations of a given set of atom-centered basis functions (the LCAO expansion). Therefore, the starting point of a calculation is the selection of an atomic basis set. The choice of types of functions (1s, 2p, 3d, etc.) on the different atomic centers and their exponents will be very important for the accuracy of the calculation. Properties not included in the basis set, for example the diffuse nature of an excited state, will obviously not be recovered even in an extended CI calculation. In some standard cases there is enough experience available to make the choice of basis

set almost a technical problem. In general, however, a deep insight into the chemical problem is necessary, because in practice one has to work far from the ideal complete basis set.

Once the basis set is chosen all possible one- and two-electron integrals are calculated. This is the only integral evaluation in the calculation. The rest will be pure matrix operations.

The one-electron space spanned by the basis functions is usually divided into two parts. Using the terminology of Sinanoğlu *et al.*[12] we shall call these spaces internal and external. Ideally, the internal space should include the occupied HF space and, in addition, all orbitals which are needed to describe degeneracy and near-degeneracy effects. The external space is then used to describe the effects of dynamical correlation. The internal space is usually obtained from a HF calculation, or in the case of near degeneracies, from an MC–SCF calculation. For reasons which will become clear later it is of interest to keep the internal space as small as possible. Often the use of the full external space leads to a CI expansion which is too large to be manageable. Therefore, a reduction of the external space may be necessary. This can, for example, be achieved by a transformation to natural orbitals, which have certain optimum convergence properties.[13,14] A method for obtaining approximate natural orbitals will be demonstrated in a later section.

A configuration basis set is obtained by building Slater determinants with orbitals from the internal and external set. In order to keep down the number of configurations some sort of selection can be made. One way to achieve this is to use the concept of interacting space.[15] Starting from a set of reference-state configurations, in which only internal orbitals are occupied, one includes, in the CI expansion, only configurations which have a nonvanishing Hamiltonian matrix element with at least one of the reference CSFs. This subset is called the first-order interacting space. In the general case this means that only configurations which correspond to single or double replacements in the reference states are taken into account. This gives fewer configurations than the more general concept of one or two electrons outside the internal set. Present experience indicates that the use of the first-order interacting space with an appropriate choice of reference states is an ideal approach for CI calculations. The main problem will then be to design methods that could accomplish this goal in an efficient way. At present this problem is not solved for the general case and is an area of increased research.

Configurations corresponding to three or more replacements appear, to a good approximation, only in the form of unlinked clusters.[16] It is possible to include the effect of these configurations in an approximate way, for example, by means of the coupled electron-pair approximation.[17]

For each configuration we can, in general, form a number of linearly independent Slater determinants by different choices of the spin part of the orbitals. Configuration state functions are formed by taking the linear combi-

nations of these determinants which are eigenfunctions of the total spin angular momentum operators. A number of methods for this spin projection are available and the reader is referred to the literature for more details.[18]

One of the bottlenecks with the CI method seems to be the slow convergence of the CI expansion. Even if the optimum properties of the natural orbitals are used to reduce the length of the expansion, the number of CSFs easily exceeds 10^4. The possibility to obtain accurate wave functions with this method has therefore been limited to systems containing few electrons. The CIMI method has been designed to overcome this problem and make possible CI calculations with high accuracy on larger systems as well. The method has so far been restricted to some special choices of reference states but has the potential to treat more general cases.

In order to explain what the CIMI method is we will now go back to the step in the calculation where the integrals are computed and the internal and external orbitals determined. The next step would be to set up the Hamiltonian matrix for the selected n-electron space. For CSFs constructed from orthogonal orbitals, these matrix elements are simple expressions involving one- and two-electron integrals over these orbitals.[18] The first step is therefore a transformation of all integrals, from the atomic basis to our selected orthogonal orbital basis. Having performed this transformation and having selected the CSFs, we then need the explicit expressions that resolve the Hamiltonian matrix elements in terms of integrals and coupling coefficients. Due to the number of matrix elements this is a formidable computational problem. Many presently used CI techniques have their main limitations in this step. When these formulas, the so-called symbolic matrix elements, have been created, it is a seemingly straightforward problem to construct the Hamiltonian matrix. An example from a calculation on the H_3 system[40] will, however, point out some of the computational difficulties. This calculation involved 20,704 CSFs, which made up a matrix of 28×10^6 nonzero elements, constructed from 3.7×10^5 integrals. Everyone familiar with such computations will realize the difficulty in constructing a matrix of that dimension.

Once the matrix is constructed the root(s) of interest should be extracted from the secular equation. For problems with more than a few hundred configurations this cannot be done with methods involving rotations of the matrix such as the Jacobi or the Givens–Householder methods. Instead, special iteration or perturbation techniques have to be applied. Both of these schemes basically lead to a multiplication of the Hamiltonian matrix with a trial wave function in the form of a vector $\mathbf{C}^{(k-1)}$ generating a vector $\boldsymbol{\sigma}^{(k)}$:

$$\boldsymbol{\sigma}^{(k)} = \mathbf{H}\mathbf{C}^{(k-1)} \tag{3}$$

A new trial wave function is constructed from $\boldsymbol{\sigma}^{(k)}$ through simple algebra, and the procedure is repeated until convergence. These iteration and perturbation schemes will be discussed in more detail in a later section. The key of the CIMI

method lies in the simple expression (3). As the Hamiltonian matrix elements are linear combinations of one- and two-electron integrals, it must obviously be possible, in principle, to formulate expressions for the vector $\boldsymbol{\sigma}^{(k)}$ directly in terms of these integrals, thereby avoiding all reference to the huge Hamiltonian matrix. A formula representing the increment to the element i of the vector $\boldsymbol{\sigma}$ from a particular integral $(ab|cd)$ of the type

$$\Delta\sigma_i^{(k)} = A\,(ab|cd)C_j^{(k-1)} \tag{4}$$

where A is a coupling coefficient depending on the spin-symmetry of the involved CSFs, will therefore form the basis for the CIMI method.

In the following sections the crucial coupling coefficients A and the diagonalization schemes will be discussed in somewhat more detail.

2.2. Coupling Coefficients

In a general case Eq. (4) may be very complicated. The problem that has to be solved for a chosen well-defined CI scheme, is to break up (4) into pieces and to find easy to use algorithms for each piece. There may be many ways of attacking this problem,[51] but we will only discuss the methods used in the MOLECULE-CI package. The integrals are divided into types and each type of integral contributes to the interaction between classes of configuration states. The definition of integral type is connected with the division of the orbitals into groups, according to their role in the CI scheme. In a general CI we will divide the orbitals into three groups. The first group contains orbitals that are fully occupied in all reference states. Only excitations *from* these orbitals are possible. The second group contains the rest of the internal orbitals. Excitations both to and from these orbitals are included. The final third group contains all the external orbitals. By definition only excitations *to* these orbitals are possible. The treatment of a fourth group containing the uncorrelated orbitals is trivial and will not be discussed further.

A two-electron integral is defined through four orbitals. One of the two factors that determine the type of integral is the division of these four orbitals into the three different groups. The other factor is the internal relationship between the indices of orbitals belonging to the same group. There are, as shown in Table 1, fourteen different integral types with all four orbitals belonging to the same group. With a closed-shell reference state there are 53 different integral types. If the reference state has one open shell, 46 new integral types appear due to the introduction of the second internal orbital group. If this group is increased by just one other orbital another 59 integral types are added making a total of 148 types. For each integral type, algorithms defining the interacting classes of configuration states have to be found. This is usually no serious problem for each type, but these algorithms may be

Table 1. The 14 Different Types of Integrals (ab/cd) Obtained When All Orbitals Belong to the Same Group

Type number	Index relations	Type number	Index relations
1	$a = b = c = d$	8	$c = d, b < c$
2	$a = b = c$	9	$a = c$
3	$b = c = d$	10	$b = d$
4	$a = b, c = d$	11	$b = c$
5	$a = c, b = d$	12	$b > c$
6	$a = b$	13	$b < c, b > d$
7	$c = d, b > c$	14	$b < d$

complicated to use. Also the large number of different types set up limits to when this procedure is useful in practice. One way to reduce this number is to reduce the number of orbital groups. When all possible configuration states are formed (complete CI) all orbitals are treated equally and therefore form only one group, the second in our definition. In this case there will consequently be only fourteen different integral types (see Table 1). A complete CI in the internal space only, reduces the number of orbital groups from three to two. The first internal group is now included in the second. The thereby introduced extra configurations could be deleted by use of the index list (discussed in a later section). The size of the index list will, however, increase rapidly and form a new limitation to the possible size of the calculation. A different way of simplifying the work required in using the CIMI method is to consider only certain classes of configuration states in the reference space, for example, only closed-shell states. This will, besides reducing the number of integral types, also make the algorithms for each integral simpler than they would be in the general case.

Returning to Eq. (4), a specified interaction between two configuration state functions through an integral type requires a coupling coefficient. This coefficient will depend on the spin coupling of the interacting configuration states and the permutation that lines up equal orbitals in these configuration states. A brute force method for obtaining the coupling coefficients was used for the case of complete CI on three valence electrons. A representative list of configuration states was fed into a computer program, which constructed formal matrix elements of the Hamiltonian operator.[20] A search for a selected integral type was then made through the list of matrix elements. Three indices will, in this case, define a particular configuration and six indices will therefore define the interaction. Four of these indices, two from each configuration, will be the same as the indices of the integral and will here be denoted as the fixed indices. If the integral contains four different indices, the remaining third index for each configuration will be called a running index. The classes of interacting configurations are therefore generated by letting the running index loop over all n orbitals. As there are n^4 integrals, full CI for three electrons will be an n^5

process. Similarly, it is easily seen that for complete CI with m electrons the number of operations will be proportional to n^{m+2}.

For double replacements from a single reference state each replacement is defined by four indices, and the interaction is described by eight indices. Four of these, two from each configuration, have to be fixed indices defining the integral, and the remaining two running indices for the configurations have to match. Simple algorithms for the interacting classes of configurations can therefore be constructed with two fixed indices and two running indices. This will also be demonstrated in a later section.

Once these algorithms have been determined we are able to express the coupling coefficients in (4) in a formal way through general expressions. Two different ways of describing the coupling coefficients have been used. One is the straightforward way, as illustrated in Table 2 for complete CI on three electrons. These coupling tables are directly obtainable through simple computer programs. For a particular type of integral Table 2 shows both the algorithm used to describe the classes of interacting configuration states and the coupling coefficient that should be used when the running index loops over all orbitals. This is precisely what is needed to use Eq. (4) in practice, and is a useful description but gives no hints to any possible generalization of the formulas. Another method has been used for the case of all single and double replacements from a single closed-shell reference state. Through a few coupling tables it is possible to formulate an expression for the increment to σ which is general for all types of integrals. This formula and the coupling tables will be described later in the section on the CIMI method for closed-shell systems. However, in spite of the generality of this formula it is the other procedure that generates the most useful description in a particular case.

Table 2. Full CI for Three Electrons. Coupling Coefficient Tables for Integral $(ab|cd)$ Where $c > b > d$ (Type 13 of Table 1)[a]

Spin coupling	$k \rightarrow$								
	d		b		c		a		
	Interaction elements $(kda^{(1,2)}\|kbc^{(1,2)})$[b]								
$(1\|1)$	$+\frac{1}{2}$	0	$-\frac{1}{2}$	$-\sqrt{6}/2$	-1	$+\sqrt{6}/2$	$-\frac{1}{2}$	0	$+\frac{1}{2}$
$(1\|2)$	$-\sqrt{3}/2$	$-\sqrt{2}$	$-\sqrt{3}/2$	0	0	0	$+\sqrt{3}/2$	$-\sqrt{2}$	$+\sqrt{3}/2$
$(2\|1)$	$-\sqrt{3}/2$	0	$+\sqrt{3}/2$	$+\sqrt{2}/2$	0	$+\sqrt{2}/2$	$-\sqrt{3}/2$	0	$+\sqrt{3}/2$
$(2\|2)$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	0	$+1$	0	$-\frac{1}{2}$	0	$-\frac{1}{2}$
	Interaction elements $(kca^{(1,2)}\|kdb^{(1,2)})$[b]								
$(1\|1)$	$+1$	$+\sqrt{6}/2$	$+\frac{1}{2}$	0	$-\frac{1}{2}$	0	$+\frac{1}{2}$	$-\sqrt{6}/2$	$+1$
$(1\|2)$	0	0	$+\sqrt{3}/2$	0	$-\sqrt{3}/2$	$-\sqrt{2}$	$-\sqrt{3}/2$	$+\sqrt{3}/2$	0
$(2\|1)$	0	$+\sqrt{2}/2$	$+\sqrt{3}/2$	$-\sqrt{2}$	$+\sqrt{3}/2$	0	$-\sqrt{3}/2$	0	0
$(2\|2)$	$+1$	0	$-\frac{1}{2}$	0	$-\frac{1}{2}$	0	$-\frac{1}{2}$	0	$+1$

[a] The entries in columns 2–10 correspond to various values of the running index k, e.g., for the entries under d the running index k equals d; for the entries in the next column (between d and b) we have $d < k < b$; etc.
[b] k is the running index and the superindex denotes spin coupling.

2.3. Diagonalization Schemes

As was pointed out earlier, extraction of roots and energies of equation system (2) has to be done either by iterative techniques or by perturbation theory, due to the usually long expansion (1), running into several thousand configuration states. These two approaches are essentially equivalent computationally, but formally differ slightly. Both of them can basically be made to require the construction of a vector $\boldsymbol{\sigma}$ according to (3). We should also mention here that some of the diagonalization techniques most frequently used today[21,22] cannot be used in their original form in connection with the CIMI method as they require a differently constructed $\boldsymbol{\sigma}$. We will start the discussion of diagonalization procedures with the perturbation techniques, and especially treat the particular scheme that has been found most efficient in connection with the CIMI method, even in comparison with general iterative techniques.

The perturbation equations are obtained by making the usual splitting of the Hamiltonian,

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{5}$$

and the expansions of the wave function and energy

$$\Psi = \sum_n \Psi^{(n)} \tag{6}$$

$$E = \sum_n \varepsilon_n \tag{7}$$

and then substituting these expressions into the Schrödinger equation. Collecting terms of order k, leads to

$$(E_0 - \hat{H}_0)\Psi^{(k)} = \hat{V}\Psi^{(k-1)} - \sum_{n=0}^{k-1} \varepsilon_{k-n} \Psi^{(n)} \tag{8}$$

If a simple expression is wanted for the components of $\Psi^{(n)}$ an $\hat{H}_0$ is needed which gives a simple inverse of $(E_0 - \hat{H}_0)$. A diagonal representation of this operator is therefore an advantage. If we make an expression of the perturbation functions into orthogonal configuration state functions $|\Phi_\mu\rangle$, a diagonal $(E_0 - \hat{H}_0)$ is, for example, obtained by

$$\hat{H}_0 = \sum_\mu |\Phi_\mu\rangle\langle\Phi_\mu|\hat{H}|\Phi_\mu\rangle\langle\Phi_\mu| \tag{9}$$

where the sum is over all configuration state functions in the basis set. In component form, (8) is then written as

$$C_\mu^{(k)} = \frac{1}{E_0 - H_{\mu\mu}} \left[\sum_{\nu=1}^{N} V_{\mu\nu} C_\nu^{(k-1)} - \sum_{n=0}^{k-1} \varepsilon_{k-n} C_\mu^{(n)} \right] \tag{10}$$

The first term inside the brackets is recognized as being basically equal to the vector component σ_μ defined by (3). The expressions for the perturbation energies obtained simultaneously as the perturbation functions $\Psi^{(k)}$ are harder to derive, and the reader is referred to Ref. 23 for details. The final formulas are

$$\varepsilon_{2k-1} = \sum_{\mu=1}^{N} C_\mu^{(k-1)} \sum_{\nu=1}^{N} V_{\mu\nu} C_\nu^{(k-1)} - \sum_{m=1}^{k-1} \sum_{n=1}^{k-1} \varepsilon_{2k-1-m-n} \sum_\mu C_\mu^{(m)} C_\mu^{(n)}$$

$$\varepsilon_{2k} = \sum_{\mu=1}^{N} C_\mu^{(k)} \sum_{\nu=1}^{N} V_{\mu\nu} C_\nu^{(k-1)} - \sum_{m=1}^{k} \sum_{n=1}^{k-1} \varepsilon_{2k-m-n} \sum_\mu C_\mu^{(m)} C_\mu^{(n)}$$

(11)

The components σ_μ are found also in these expressions. Equations (10) and (11) can be used together with the linear expressions (6) and (7) until convergence is reached. A better procedure [24] is to solve the secular equation in terms of the perturbation functions $\Psi^{(k)}$. As the vectors $\sigma^{(k)}$, according to (3), are constructed in each iteration, a single scalar product of the previously obtained perturbation functions will automatically yield the full Hamiltonian matrix in terms of these functions. These matrix elements may also be written in closed form,[23]

$$\langle \Psi^{(p)} | \hat{H} | \Psi^{(q)} \rangle = \langle \Psi^{(p)} | \hat{H}_0 | \Psi^{(q)} \rangle + \varepsilon_{p+q+1} + \sum_{k=1}^{p} \sum_{l=1}^{q} \varepsilon_{p+q+1-l-k} \langle \Psi^{(k)} | \Psi^{(l)} \rangle$$

(12)

After n iterations a secular problem of dimension $(n-1)$ is easily set up and solved by standard techniques. This method, in Table 3, is referred to as nonlinear variation perturbation theory. Other ways of obtaining improved convergence on the energy involve using the $[N, N-1]$ and $[N, N]$ Padé approximants to extrapolate the perturbation energies. For more details on this approach, including closed expressions for the approximants, the reader is referred to Refs. 24 and 25. Finally, the variational energy from a linear summation of the perturbation functions is also easily calculated from simple closed formulas.[23] This method is shown in Table 3, and is referred to as linear

Table 3. Convergence Properties of Different Perturbative Methods for Solving the CI Equations[a]

Iteration	Linear perturbation theory (ε_{2n})	Linear variation perturbation theory	Nonlinear variation perturbation theory	$[N, N-1]$ Padé approximation	$[N, N]$ Padé approximation
2	−0.413239	−0.242832	−0.267611	−0.337680	−0.356097
4	−0.239193	−0.279266	−0.313136	−0.342975	−0.386712
6	−0.137370	−0.133265	−0.320340	−0.324810	−0.325122
8	−2.105398	−0.180377	−0.320674	−0.324273	−0.310087
9	−2.758177	−0.056128	−0.320685	−0.319864	−0.322604
10	7.954382	0.047972	−0.320688	−0.321207	−0.320586

[a]The example illustrated refers to a calculation on the HF molecule with $d(HF) = 4.0$ a.u. and 971 configurations.

variation perturbation theory. All these methods have been compared to each other and results from a representative case [a calculation on HF with d (HF) = 4.0 a.u.] are shown in Table 3. The nonlinear variation perturbation approach has always been found superior, and convergence to six decimal places in the correlation energy for a ground state is usually obtained in 6–7 iterations. Very rarely are up to 10 iterations needed. The iterative techniques described below have shown inferior convergence properties. However, a certain flexibility in both the iterative and the perturbation techniques has not yet been fully explored, so the question of which is the most efficient diagonalization method in connection with the CIMI method is still not completely answered. In perturbation theory this flexibility appears in the choice of $\hat{H}_0$. The matrix elements $\langle \Phi_\mu | \hat{H} | \Phi_\mu \rangle$ appearing in (9) can be replaced by arbitrary constants α_μ, making up a still-diagonal $\hat{H}_0$ of the form

$$\hat{H}_0 = \sum_\mu |\mu\rangle \alpha_\mu \langle\mu| \tag{13}$$

There does not seem to be any theoretically based best choices of $\hat{H}_0$. By diagrammatic arguments the choice (9) has been inferred based on inherent summation to higher order. However, this does not seem to be connected with faster convergence properties. On the contrary, better convergence has so far been obtained choosing α_μ equal to diagonal elements of a sum of Fock operators

$$\hat{H}_0 = \sum_\mu |\mu\rangle\langle\mu| \hat{F} |\mu\rangle\langle\mu| \tag{14}$$

where $\hat{F} = \sum_{i=1}^n \hat{f}(i)$ and $\hat{f}$ is a Hartree–Fock type operator.

Finally, we should mention that the variation perturbation approach is also well suited for convergence on excited states.[26] However, this has still not been used with the CIMI method. A similar approach has recently been suggested by Davidson[27] and seems to compete well even with optimally constructed iterative techniques.

An iterative solution of an equation system of the type

$$\mathbf{A} \cdot \mathbf{C} = 0 \tag{15}$$

starts with the division of the matrix $\mathbf{A}$ into two parts

$$\mathbf{A} = \mathbf{A}' + \mathbf{A}'' \tag{16}$$

Moving $\mathbf{A}' \cdot \mathbf{C}$ to the right-hand side and operating to the left with $\mathbf{A}''^{-1}$ sets up the general iterative scheme

$$\mathbf{C}^{(k)} = -\mathbf{A}''^{-1} \cdot \mathbf{A}' \cdot \mathbf{C}^{(k-1)} \tag{17}$$

which is then carried till convergence. In order for this scheme to be practically useful $\mathbf{A}''$ should be diagonal, so that the inverse is easily constructed. Therefore, $\mathbf{A}''$ is taken as the whole or part of the diagonal elements of $\mathbf{A}$. In the

former case, as applied to the equation system (2) with an orthogonal basis set, we get, in component form,

$$A''_{\mu\nu} = (H_{\mu\mu} - E)\,\delta_{\mu\nu}$$

$$A'_{\mu\nu} = H_{\mu\nu}(1 - \delta_{\mu\nu})$$

which leads to

$$C_\mu^{(k)} = \frac{1}{E^{(k-1)} - H_{\mu\mu}}\left[\sum_{\nu=1}^{N} H_{\mu\nu}C_\nu^{(k-1)} - H_{\mu\mu}C_\mu^{(k-1)}\right]$$

or more commonly written as

$$\Delta C_\mu^{(k)} = \frac{1}{E^{(k-1)} - H_{\mu\mu}}\left[\sum_{\nu=1}^{N} H_{\mu\nu}C_\nu^{(k-1)} - E^{(k-1)}C_\mu^{(k-1)}\right] \tag{18}$$

where the energy is simultaneously updated by

$$E^{(k-1)} = \sum_{\mu=1}^{N} C_\mu^{(k-1)} \sum_{\mu=1}^{N} H_{\mu\nu}C_\nu^{(k-1)} \bigg/ \sum_{\mu=1}^{N} [C_\mu^{(k-1)}]^2 \tag{19}$$

The basic operation (3) is recognized in both (18) and (19). Various modifications of the updating form (18) can be obtained by choosing the splitting differently in (16). A more general division of A than was done in (18) leads to the denominator $E^{(k-1)} - H_{\mu\mu} - \alpha'_\mu$ instead, where α'_μ can be chosen to speed up the convergence [no other change in (18) is made by this modification]. This flexibility corresponds to the equivalent freedom of choosing $\hat{H}_0$ in the perturbation technique. Similar techniques of shifting denominators have been used in Hartree–Fock[28] and MC–SCF calculations.[29,30]

2.4. Approximate Natural Orbitals

We mentioned earlier that in many cases a truncation of the external orbital space is desired in order to make the CI expansion shorter. With a given truncation the so-called natural spin orbitals[13] will, in a certain respect, be the optimal choice as an orbital set. The natural spin orbitals are defined as the orbitals that diagonalize the first-order reduced density matrix which, with a CI expansion of type (1), has the form

$$\rho_1(x'_1; x_1) = \sum_\mu \sum_\nu C_\mu^* C_\nu \rho_1(\mu\nu|x'_1 x_1) \tag{20}$$

where

$$\rho_1(\mu\nu|x'_1 x_1) = n \int \Phi_\mu^*(x'_1 x_2 \cdots x_n)\Phi_\nu(x_1 x_2 \cdots x_n)\,d\tau_2 \cdots d\tau_n$$

is called the transition density matrix. The density matrix may be represented in terms of the spin-orbitals $\psi_p(x)$, according to

$$\rho_1(x', x) = \sum_{p,q} D_{pq} \psi_p^*(x') \psi_q(x) \tag{21}$$

where the sum runs over all orbitals in the internal and external set. The useful theorem that can be rigorously proved for the natural spin-orbitals[14] states that the expansion of a trial wave function Φ in a natural spin-orbital basis minimizes the least-square deviation Δ:

$$\Delta = \langle \Psi - \Phi | \Psi - \Phi \rangle$$

where Ψ is the exact wave function.

As the first-order reduced density matrix and consequently the natural orbitals are constructed from the exact wave function, some approximation to this matrix has to be used in practice. Various methods for constructing approximate density matrices have for some time been used by different groups.[31–33] Some of these schemes are essentially based on perturbation theory. The components of the external part of the density matrix can be constructed to second order from a wave function known only to first order. As can be seen from (8) the expressions for the coefficients of the first-order wave function are simple and can therefore be easily constructed. The Hamiltonian matrix elements needed are those that connect the external space with the reference space and, depending on the $\hat{H}_0$ chosen, possibly also the diagonal elements. In this context we should remind the reader that a result obtained from finite-order perturbation theory, as in this case the wave function to first order, is only well defined with respect to a certain splitting of the Hamiltonian into $\hat{H}_0 + \hat{V}$. In fact, by choosing $\hat{H}_0$ according to (13) any result for the wave function and consequently the density matrix can be obtained due to the freedom of choice of α_μ. The usefulness of approximate natural orbitals constructed by perturbation theory therefore has to be empirically judged. Orbitals that seem to give reasonable convergence properties are obtained by choosing $\hat{H}_0$ according to (9) or (14). We have used the latter $\hat{H}_0$. For the case of a single closed-shell reference state, a simple formula for the *external elements* of the first-order density matrix in terms of molecular integrals are obtained to second order:

$$D_{ab}^{(2)} =$$

$$\sum_{i,j}^{occ} \sum_{c}^{ext} \frac{2(ai|cj)(bi|cj) + 2(aj|ci)(bj|ci) - (ai|cj)(bj|ci) - (aj|ci)(bi|cj)}{(\varepsilon_c + \varepsilon_a - \varepsilon_i - \varepsilon_j)(\varepsilon_c + \varepsilon_b - \varepsilon_i - \varepsilon_j)} \tag{22}$$

where a, b, and c denote external orbitals, i, j internal orbitals, and ε are the orbital energies. This formula is essentially equivalent to that obtained by

diagrammatic techniques and by Green's function theory.[33] By ordering the integrals in a specific order, the density matrix can be constructed directly from one pass through the integrals. This technique is similar in spirit to the CIMI method itself, where the long list of Hamiltonian matrix elements are avoided in going from $C^{(n-1)}$ to $\sigma^{(k)}$. Here the long list of wave function coefficients is avoided in going from the integrals to the short list of density matrix elements. The method is possible to extend and keep efficient to at least some more general cases with a multiconfigurational reference space. The by far most time-consuming step in the construction of these approximate natural orbitals will be the required transformation of the integrals. By using the fact that only certain integrals are needed in (22) we can reduce the transformation time substantially. Further, the transformation should optimally proceed in the following order:

$$(pi|rs) = \sum_q C_{iq}(pq|rs)$$

$$(pi|rj) = \sum_s C_{js}(pi|rs)$$

$$(ai|rj) = \sum_p C_{ap}(pi|rj)$$ (23)

$$(ai|bj) = \sum_r C_{br}(ai|rj)$$

where the same convention as in (22) has been used for the indices. The rate-determining step will be the first summation in (23). If the number of internal orbitals is N_{int} and the total number of orbitals is N_{tot}, the ratio between the number of operations here and the corresponding full transformation is N_{int}/N_{tot}, which will usually be a small number. The number of operations in the other three summations in (23) will be reduced even further.

   Convergence on the correlation energy with different orbital sets is illustrated in Fig 1 from a study on the water molecule. A basis set of essentially
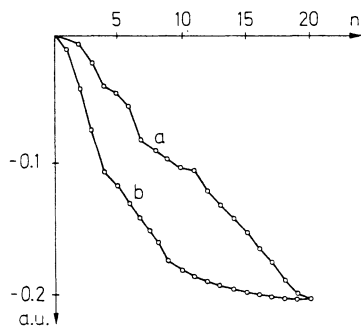

Fig. 1. Correlation energy for H_2O (equlilbrium geometry) as a function of the number of external orbitals. Curve a is obtained with virtual canonical HF orbitals ordered by increasing orbital energy; curve b with natural or approximate natural orbitals ordered by decreasing occupation numbers.

double zeta plus polarization quality was used and the $1s$ orbital on the oxygen was left uncorrelated. Three sets of orbitals are compared, the *canonical SCF orbitals* (COs) ordered with respect to orbital energies, the *approximate natural orbitals* (ANOs) obtained from (22), and the *natural orbitals* (NOs) obtained from the converged CI calculation with all canonical orbitals. The latter two sets are ordered with respect to occupation numbers. As could have been expected from the above theorem, we see that the NO expansion converges much quicker on the correlation energy than the CO expansion (the ANO expansion yields results so similar to those obtained with the NO expansion that they cannot be distinguished on the scale used in Fig. 1). This is not obvious, however, as the theorem states something about the overlap and not the energy. If the core has been correlated, for example, selection principles other than high occupation numbers would have to have been considered.[34] What is demonstrated in Fig. 1, is that if a certain number of orbitals are taken out from the orbital set when correlating the valence shells, less correlation energy is lost if the orbitals are ANOs than if they are COs. However, in practice the interest is not so much in the correlation energy itself as in a particular chemical property, for example, an equilibrium bond distance. What is wanted in this case is an *equal* loss of correlation energy for *different* distances. For an ordinary chemical bond a loss of valence shell correlation energy will usually be proportional to the loss of accuracy on the bond distance. For a van der Waals interaction, however, good results can be obtained by neglecting the intraatomic correlation completely, though this is orders of magnitude larger than the interaction energy itself.[35,36] A different truncation for intra- and interatomic correlation is therefore recommended in this case.[56] In general, a division of a problem into different chemical effects may allow a more severe truncation of the orbital set and thereby yield a more efficient calculation.

3. Application to Some Different Types of CI Expansions

3.1. A Closed-Shell Single-Determinant Reference State

The direct CI method from molecular integrals was first applied to systems with one closed-shell reference state,[8] including in the CI expansion all single- and double-replacement states with respect to the reference state:

$$\Psi = \Phi_0 + \sum_i \sum_a C_{i \to a} \Phi_{i \to a} + \sum_{i>j} \sum_{a>b} C_{ij \to ab} \Phi_{ij \to ab} \tag{23}$$

where Φ_0 is the reference state function, Φ_i^a represents a single-replacement state, and Φ_{ij}^{ab} a double-replacement state. Indices $i, j, \ldots$ are, as before, used to denote orbitals occupied in Φ_0 (internal orbitals), while $a, b, \ldots$ are used for

the remaining orbital space (external orbitals). The state functions should be spin eigenfunctions corresponding to a singlet state.

Spin eigenfunctions can be obtained in a number of different ways. The state functions used in the CI expansion (23) have been chosen to have the following form:

$$\Phi_i^a = \sqrt{2}\hat{O}[\dots \varphi_i\bar{\varphi}_a \dots] \tag{24a}$$

$$\Phi_{ii}^{aa} = [\dots \varphi_a\bar{\varphi}_a \dots] \tag{24b}$$

$$\Phi_{ij}^{aa} = \sqrt{2}\hat{O}[\dots \varphi_i\bar{\varphi}_a \dots \varphi_a\bar{\varphi}_j \dots] \tag{24c}$$

$$\Phi_{ii}^{ab} = \sqrt{2}\hat{O}[\dots \varphi_a\bar{\varphi}_b \dots] \tag{24d}$$

$$^1\Phi_{ij}^{ab} = -\sqrt{3}\hat{O}[\dots \varphi_i\varphi_a \dots \bar{\varphi}_b\bar{\varphi}_j \dots] \tag{24e}$$

$$^2\Phi_{ij}^{ab} = \hat{O}\{[\dots \varphi_i\bar{\varphi}_a \dots \varphi_j\bar{\varphi}_b \dots] + [\dots \varphi_a\bar{\varphi}_i \dots \varphi_j\bar{\varphi}_b \dots]\} \tag{24f}$$

where the square brackets are used to denote a normalized determinant. Only the replacements are shown explicitly. $\hat{O}$ is a spin-projection operator for singlet states:

$$\hat{O} = \prod_{S \neq 0}\left[1 - \frac{\hat{S}^2}{S(S+1)}\right] \tag{25}$$

The state functions (24a)–(24f) should belong to the totally symmetric representation of the molecular point group. The treatment of symmetry is considerably simplified by allowing only point groups with one-dimensional irreducible representations. For some molecules this will mean that only a subgroup of the full symmetry group can be used. The state functions are then automatically symmetry adapted, provided that symmetry-adapted one-electron orbitals are used. The condition for a configuration state $\Phi_{ijk\dots}^{abc\dots}$ to belong to the same representation as reference state Φ_0 of arbitrary symmetry is that the product of the orbitals in the replacement belongs to the totally symmetric representation Γ_1. For one-dimensional groups this means that

$$\gamma_i \times \gamma_j \times \gamma_k \times \cdots \times \gamma_a \times \gamma_b \times \gamma_c \times \cdots = \Gamma_1 \tag{26}$$

where γ_ν is the irreducible representation for orbital ν.

Using the state functions given above we can construct 21 different types of matrix elements of the Hamiltonian $\hat{H}$. All these elements can be written as linear combinations of one- and two-electron integrals. To simplify these expressions the Hamiltonian is first partitioned into a Hartree–Fock operator $\hat{F}$

and a fluctuation potential $\hat{V}$:

$$\hat{H} = \hat{F} + \hat{V} \tag{27}$$

where

$$\hat{F} = \sum_{i=1}^{2m} \hat{f}(i)$$

with

$$\hat{f}(i) = \left\{ \hat{h}(i) + \sum_{j=1}^{m} [2\hat{J}_j(i) - \hat{K}_j(i)] \right\} \tag{28}$$

and

$$\hat{V} = \sum_{i<j} (1/r_{ij}) - \sum_{i=1}^{2m} \sum_{j=1}^{m} [2\hat{J}_j(i) - K_j(i)] \tag{29}$$

where $\hat{h}$ is the one-electron operator and $\hat{J}_j$ and $\hat{K}_j$ are the ordinary Coulomb and exchange operators; m is the number of doubly occupied orbitals in the reference state Φ_0.

As was pointed out in the preceding section, the most crucial point in a CI calculation is the evaluation of the quantity

$$\sigma_\mu = \sum_\nu (H_{\mu\nu} - H_{00} \delta_{\mu\nu}) C_\nu \tag{30}$$

By using (27) this quantity can be written as

$$\sigma_\mu = \sum_\nu (F_{\mu\nu} - F_{00} \delta_{\mu\nu}) C_\nu + \sum_\nu (V_{\mu\nu} - V_{00} \delta_{\mu\nu}) C_\nu \tag{31}$$

where $F_{\mu\nu}$ and $V_{\mu\nu}$ are matrix elements of the operators $\hat{F}$ and $\hat{V}$, respectively. Characteristic for the CIMI method is the resolution of the second sum in (31) in terms of molecular two-electron integrals. Define the integrals

$$f_{pq} = \int \varphi_p^*(1)\hat{f}(1)\varphi_q(1) \, dV_1 \tag{32}$$

$$(pq|rs) = \int \varphi_p^*(1)\varphi_q(1)(1/r_{12})\varphi_r^*(2)\varphi_s(2) \, dV_1 \, dV_2 \tag{33}$$

The vector $\boldsymbol{\sigma}$ can be written as a sum over these one- and two-electron integrals multiplied with appropriate coupling coefficients which depend only on the spin couplings for the corresponding configuration state functions. For a double-replacement state ($\mu = ij \rightarrow ab$) we obtain the following contribution to

σ_μ from the interaction with all double-replacement states:

$$\Delta\sigma_{ij\to ab} = \sum_c j_2(\mu,\nu)\{f_{bc}C_{ij\to ac} + f_{ac}C_{ij\to cb}\}$$

$$-\sum_k j_1(\mu,\nu)\{f_{kj}C_{ik\to ab} + f_{ik}C_{kj\to ab}\}$$

$$+\sum_{k\geq l}\{j_1(\mu,\nu)(ik|jl) + k_1(\mu,\nu)(il|kj)\}C_{kl\to ab}$$

$$+\sum_{c\geq d}\{j_2(\mu,\nu)(ac|bd) + k_2(\mu,\nu)(ad|bc)\}C_{ij\to cd}$$

$$+\sum_{k,c}\{j_3(\mu,\nu)(ac|ik) + k_3(\mu,\nu)(ai|ck)\}C_{kj\to cb}$$

$$+\sum_{k,c}\{j_4(\mu,\nu)(bc|jk) + k_4(\mu,\nu)(bj|ck)\}C_{ik\to ac}$$

$$+\sum_{k,c}\{j_5(\mu,\nu)(bc|ik) + k_5(\mu,\nu)(bi|ck)\}C_{kj\to ac}$$

$$+\sum_{k,c}\{j_6(\mu,\nu)(ac|jk) + k_6(\mu,\nu)(aj|ck)\}c_{ik\to cb} \tag{34}$$

The coupling constants $j_i(\mu,\nu)$ and $k_i(\mu,\nu)$ depend only on the spin coupling appropriate for the state functions Φ_μ and Φ_ν, and on the signature of permutations which bring equal indices into equal positions. They take simple numerical values (Table 4).

From the interaction with single-replacement states we obtain the following contribution:

$$\Delta\sigma_{ij\to ab} = i_1(\mu)f_{bj}C_{i\to a} + i_2(\mu)f_{aj}C_{i\to b}$$

$$+ i_1(\mu)f_{bi}C_{j\to a} + i_2(\mu)f_{ai}C_{j\to b}$$

$$+\sum_c\{i_1(\mu)(ac|bj) + i_2(\mu)(aj|bc)\}C_{i\to c}$$

$$+\sum_c\{i_1(\mu)(ai|bc) + i_2(\mu)(ac|bi)\}C_{j\to c}$$

$$-\sum_k\{i_1(\mu)(ai|jk) + i_2(\mu)(aj|ik)\}C_{k\to b}$$

$$-\sum_k\{i_1(\mu)(bj|ik) + i_2(\mu)(bi|jk)\}C_{k\to a} \tag{35}$$

Table 4. Coupling Constants for Interactions between Double Replacement CSFs in the CICS Case [a]

$J_1(\mu, \nu)$

μ	1	2	3	4	5
1	1	$\tfrac{1}{2}\sqrt{2}$	—	—	—
2	$\sqrt{2}$	1	—	—	—
3	—	—	1	$\tfrac{1}{2}\sqrt{\tfrac{3}{2}}$	$\tfrac{1}{2}\sqrt{\tfrac{1}{2}}$
4	—	—	$\sqrt{\tfrac{3}{2}}$	1	0
5	—	—	$\sqrt{\tfrac{1}{2}}$	0	1

$K_1(\mu, \nu)$

μ	1	2	3	4	5
1	0	$\tfrac{1}{2}\sqrt{2}$	—	—	—
2	0	1	—	—	—
3	—	—	0	$\tfrac{1}{2}\sqrt{\tfrac{3}{2}}$	$\tfrac{1}{2}\sqrt{\tfrac{1}{2}}$
4	—	—	0	$\tfrac{1}{2}$	$\sqrt{3}/2$
5	—	—	0	$\sqrt{3}/2$	$-\tfrac{1}{2}$

$J_2(\mu, \nu)$

μ	1	2	3	4	5
1	1	—	$\tfrac{1}{2}\sqrt{2}$	—	—
2	—	1	—	$\tfrac{1}{2}\sqrt{\tfrac{3}{2}}$	$\tfrac{1}{2}\sqrt{\tfrac{1}{2}}$
3	$\sqrt{2}$	—	1	—	—
4	—	$\sqrt{\tfrac{3}{2}}$	—	1	0
5	—	$\sqrt{\tfrac{1}{2}}$	—	0	1

$K_2(\mu, \nu)$

μ	1	2	3	4	5
1	0	—	$\tfrac{1}{2}\sqrt{2}$	—	—
2	—	0	—	$\tfrac{1}{2}\sqrt{\tfrac{3}{2}}$	$\tfrac{1}{2}\sqrt{\tfrac{1}{2}}$
3	0	—	1	—	—
4	—	0	—	$\tfrac{1}{2}$	$\sqrt{3}/2$
5	—	0	—	$\sqrt{3}/2$	$-\tfrac{1}{2}$

$J_3(\mu, \nu)$

μ	1	2	3	4	5
1	-4	$-2\sqrt{2}$	$-2\sqrt{2}$	$-\sqrt{3}$	-1
2	$-2\sqrt{2}$	-2	-2	$-\sqrt{\tfrac{3}{2}}$	$-\sqrt{\tfrac{1}{2}}$
3	$-2\sqrt{2}$	-2	-2	$-\sqrt{\tfrac{3}{2}}$	$-\sqrt{\tfrac{1}{2}}$
4	$-\sqrt{3}$	$-\sqrt{\tfrac{3}{2}}$	$-\sqrt{\tfrac{3}{2}}$	$-(3+p)/4$	$\sqrt{3}(p-1)/4$
5	-1	$-\sqrt{\tfrac{1}{2}}$	$-\sqrt{\tfrac{1}{2}}$	$\sqrt{3}(p-1)/4$	$-(1+3p)/4$

$K_3(\mu, \nu)$

μ	1	2	3	4	5
1	2	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{3}(1-p)/2$	$(1+3p)/2$
2	$\sqrt{2}$	1	1	$\sqrt{6}(1-p)/4$	$\sqrt{2}(1+3p)/4$
3	$\sqrt{2}$	1	1	$\sqrt{6}(1-p)/4$	$\sqrt{2}(1+3p)/4$
4	0	0	0	0	0
5	2	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{3}(1-p)/2$	$(1+3p)/2$

$J_4(\mu, \nu)$

μ	1	2	3	4	5
1	0	0	0	0	0
2	$-2\sqrt{2}$	-2	-2	$-\sqrt{\tfrac{3}{2}}$	$-\sqrt{\tfrac{1}{2}}$
3	$-2\sqrt{2}$	-2	-2	$-\sqrt{\tfrac{3}{2}}$	$-\sqrt{\tfrac{1}{2}}$
4	$-\sqrt{3}$	$-\sqrt{\tfrac{3}{2}}$	$-\sqrt{\tfrac{3}{2}}$	$-(3+p)/4$	$\sqrt{3}(p-1)/4$
5	-1	$-\sqrt{\tfrac{1}{2}}$	$-\sqrt{\tfrac{1}{2}}$	$\sqrt{3}(p-1)/4$	$-(1+3p)/4$

$K_4(\mu, \nu)$

μ	1	2	3	4	5
1	0	0	0	0	0
2	$\sqrt{2}$	1	1	$\sqrt{6}(1-p)/4$	$\sqrt{2}(1+3p)/4$
3	$\sqrt{2}$	1	1	$\sqrt{6}(1-p)/4$	$\sqrt{2}(1+3p)/4$
4	0	0	0	0	0
5	2	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{3}(1-p)/2$	$(1+3p)/2$

$J_5(\mu, \nu) = J_6(\mu, \nu)$

μ	1	2	3	4	5
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	$-\sqrt{3}$	$-\sqrt{\tfrac{3}{2}}$	$-\sqrt{\tfrac{3}{2}}$	$-(3+p)/4$	$\sqrt{3}(p-1)/4$
5	-1	$-\sqrt{\tfrac{1}{2}}$	$-\sqrt{\tfrac{1}{2}}$	$\sqrt{3}(p-1)/4$	$-(1+3p)/4$

$K_5(\mu, \nu) = K_6(\mu, \nu)$

μ	1	2	3	4	5
1	0	0	0	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	$\sqrt{3}$	$\sqrt{\tfrac{3}{2}}$	$\sqrt{\tfrac{3}{2}}$	$3(1+p)/4$	$\sqrt{3}(1-3p)/4$
5	-1	$-\sqrt{\tfrac{1}{2}}$	$-\sqrt{\tfrac{1}{2}}$	$-\sqrt{3}(1+p)/4$	$(3p-1)/4$

[a] The indices (μ, ν) refer to the different types of double-replacement CSFs by Eqs. (24b)–(24f)[52] and p is the signature of the permutation which brings equal indices into equal positions in the two configurations.

Table 5. Coupling Coefficients for the Interactions between Double- and Single-Replacement CSFs in the CICS Case[a]

μ	$i_1(\mu)$	$i_2(\mu)$
1	$\sqrt{2}/4$	$\sqrt{2}/4$
2	$\frac{1}{2}$	$\frac{1}{2}$
3	$\frac{1}{2}$	$\frac{1}{2}$
4	0	$\sqrt{\frac{3}{2}}$
5	$\sqrt{2}$	$-\sqrt{\frac{1}{2}}$

[a] The indices (μ) refer to the five state functions defined in Eqs. (24b)–(24f).

with a corresponding relation for the contributions from double-replacement states to $\sigma_{i \to a}$. The coupling coefficients $i_1(\mu)$ and $i_2(\mu)$ are found in Table 5. Finally, the interaction between single-replacement states gives the contribution

$$\Delta \sigma_{i \to a} = \sum_b f_{ab} C_{i \to b} - \sum_j f_{ij} C_{j \to a} + \sum_{j,b} \{2(ai|bj) - (ab|ij)\} C_{j \to b} \qquad (36)$$

Thus we have replaced the sum over configurations with a much shorter sum over the one- and two-electron integrals. Computationally, the construction of the vector $\boldsymbol{\sigma}$ is accomplished during the sequential reading of the integral list. Each integral is identified with respect to its type as defined in Eqs. (34)–(36). It is then multiplied with a coupling constant and the contribution is added to the appropriate σ_μ terms. The necessary programming effort will strongly depend on the number of different types of two-electron integrals, since each integral type requires its own specific loop structure.

The CIMI method for closed-shell systems has been implemented as the MOLECULE-CICS program. The overall flow scheme for this program is shown in Fig. 2. The actual CI calculation is preceded by an integral evaluation and an SCF-calculation. This calculation provides the orbital set used for the construction of the configuration state functions. Usually either the canonical orbitals or approximate natural orbitals are used as constructed according to the method described in the preceding section. Other possibilities can easily be implemented, e.g., to use localized orbitals.

A transformation of the two-electron integrals has to precede the actual CI calculation. The atomic two-electron integrals are, in MOLECULE, computed directly over a symmetry-adapted orbital basis. The transformation can therefore also be symmetry blocked. This greatly reduces the necessary computational effort, since the time needed is proportional to the fifth power of the maximum number of orbitals in one irreducible representation. The transfor-
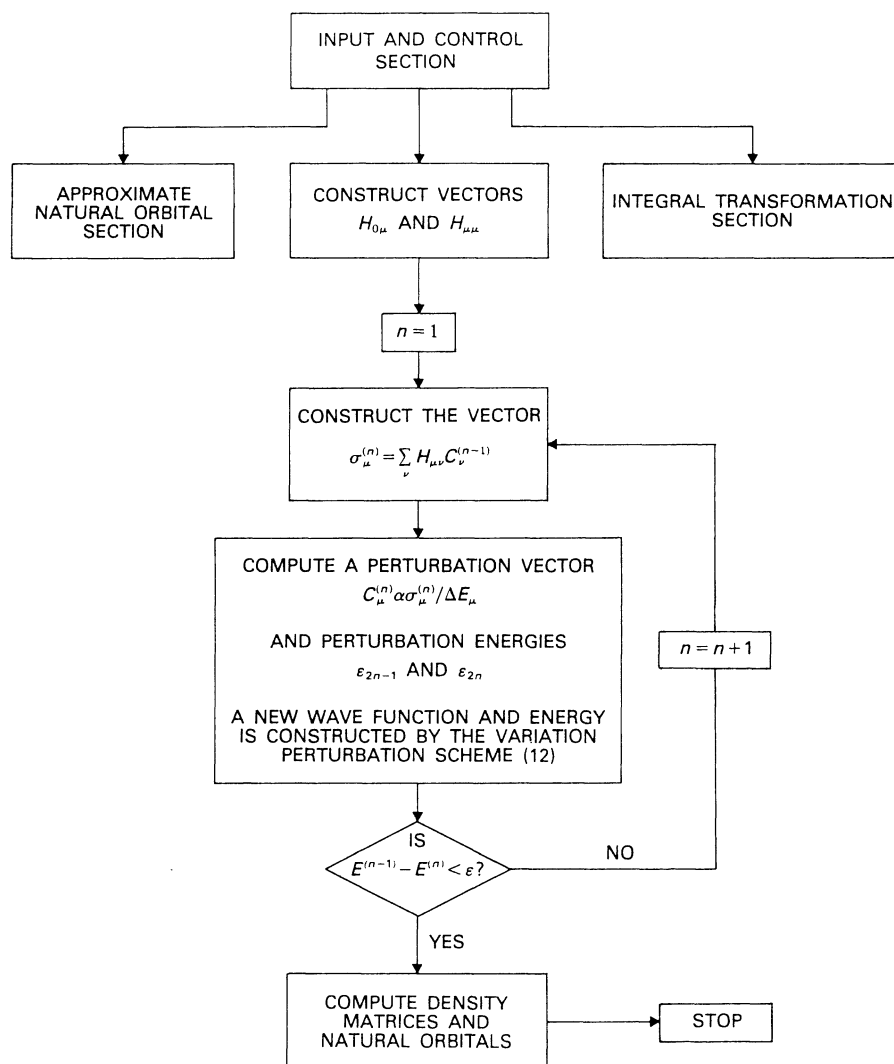
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┌─────────────────────────────┐
│      INPUT AND CONTROL       │
│          SECTION             │
└─────────────────────────────┘
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┌──────────────────┐ ┌──────────────────────┐ ┌──────────────────────────┐
│   APPROXIMATE   │ │ CONSTRUCT VECTORS   │ │ INTEGRAL TRANSFORMATION │
│ NATURAL ORBITAL │ │ $H_{0\mu}$ AND $H_{\mu\mu}$ │ │   SECTION   │
│   SECTION   │ │   │ │   │
└──────────────────┘ └──────────────────────┘ └──────────────────────────┘

┌──────────┐
│ $n = 1$ │
└──────────┘

┌──────────────────────────────┐
│   CONSTRUCT THE VECTOR   │
│   │
│ $\sigma_\mu^{(n)} = \sum_\nu H_{\mu\nu} C_\nu^{(n-1)}$ │
└──────────────────────────────┘

┌────────────────────────────────────┐
│   COMPUTE A PERTURBATION VECTOR   │
│   │
│ $C_\mu^{(n)} \alpha \sigma_\mu^{(n)}/\Delta E_\mu$ │
│   │
│   AND PERTURBATION ENERGIES   │
│   │   ┌──────────────┐
│ ε_{2n-1} AND ε_{2n} │   │ $n = n + 1$ │
│   │   └──────────────┘
│ A NEW WAVE FUNCTION AND ENERGY   │
│ IS CONSTRUCTED BY THE VARIATION   │
│ PERTURBATION SCHEME (12)   │
└────────────────────────────────────┘

                  IS
        $E^{(n-1)} - E^{(n)} < \varepsilon$?   NO

                 YES

┌──────────────────┐   ┌────────┐
│ COMPUTE DENSITY │   │ STOP │
│   MATRICES AND   │ ─────────▶ │   │
│ NATURAL ORBITALS │   └────────┘
└──────────────────┘

Fig. 2. Flow chart for the MOLECULE-CICS program.

mation is performed using the method given by Yoshimine,[37] which makes heavy use of direct access. An efficient two-electron transformation is an important part of a CI calculation since the limit in the size of the atomic orbital basis is to a large extent set by this step.

The actual CI calculation starts with a computation of the vectors $H_{0\mu}$ and optionally $H_{\mu\mu}$ for later use. This part also gives the second-order perturbation energy. The corresponding first-order CI vector may be used as a starting vector for the iterative search for an eigenvector and eigenvalue of the Hamiltonian.

The possible perturbation (or iteration) schemes have been previously discussed in detail. The by far most time consuming part in these schemes is the construction of the vector σ. To efficiently work with the vectors σ and $\mathbf{C}$ it will be necessary to quickly identify the nonzero components from the four integers, i, j, a, and b, of the replacement. For this reason an index vector is constructed. A position in this vector corresponding to the double replacement $ij \to ab$ is given by

$$N[i(i-1)/2+j]+a(a-1)/2+b$$

where N is the number of orbital pairs in the external set. This position contains either a reference to the first spin state for this configuration or a zero. If a zero is found, the corresponding state functions have been excluded from the CI expansion. This provides an easy way of excluding all configurations which are not allowed by symmetry. In the construction of the index vector it is also possible to impose other conditions on the CI expansion, e.g., to exclude all intramolecular replacements in studies of intermolecular interactions.

The iteration procedure is controlled by a convergence test which can optionally be made on either the CI vector or the correlation energy. The iteration procedure is ended when the threshold is reached, and the calculation is completed with the construction of the first-order density matrix and the natural orbitals.

3.2. Expansion in Single Determinants

The extension of the CIMI method to the general open-shell case is a difficult problem mainly due to the complicated dependence of the constants A in (4) on the spin coupling. One way to avoid most of these difficulties is to remove the spin coupling completely and instead work with single determinants. The main drawback of such a procedure will be the increased number of independent terms in the CI expansion. Due to spin symmetry, relationships exist between the coefficients for different determinants, and this can be used to make the construction of the σ vector more efficient. If single determinants are used it is, on the other hand, possible to relax the condition of pairing electrons into the same molecular orbitals and instead allow different space orbitals for different spin. This will destroy the relationships between the coefficients but it can be assumed that it will increase the convergence of the CI expansion. A determinant obtained from an *u*nrestricted *H*artree–*F*ock (UHF) calculation would in this case be allowed as the reference state. A CI program constructed from these principles, here denoted CISD, uses, like the CICS program, a basis set of all single and double replacements out of one single determinant.

The CI basis set will then consist of the following types of determinants, where we use the sign convention of ordering α-spins first:

The reference state

$$\Phi_0 = [\ldots i_\alpha j_\alpha \ldots \bar{i}_\beta \bar{j}_\beta \ldots] \tag{37}$$

Single replacements

$$\Phi_{i_\alpha}^{a_\alpha} = [\ldots a_\alpha j_\alpha \ldots \bar{i}_\beta \bar{j}_\beta \ldots] \quad (\alpha \text{ excitations})$$

$$\Phi_{i_\beta}^{a_\beta} = [\ldots i_\alpha j_\alpha \ldots \bar{a}_\beta \bar{j}_\beta \ldots] \quad (\beta \text{ excitations}) \tag{38}$$

Double replacements

$$\Phi_{i_\alpha j_\alpha}^{a_\alpha b_\alpha} = [\ldots a_\alpha b_\alpha \ldots \bar{i}_\beta \bar{j}_\beta \ldots] \quad (\alpha\alpha \text{ excitations})$$

$$\Phi_{o_\beta j_\beta}^{a_\beta b_\beta} = [\ldots i_\alpha j_\alpha \ldots \bar{a}_\beta \bar{b}_\beta \ldots] \quad (\beta\beta \text{ excitations}) \tag{39}$$

$$\Phi_{i_\alpha j_\beta}^{a_\alpha b_\beta} = [\ldots a_\alpha j_\alpha \ldots \bar{i}_\beta \bar{b}_\beta \ldots] \quad (\alpha\beta \text{ excitations})$$

In the special case of a closed-shell reference state the determinants (37)–(39) will span the same space as the projected configurations used in the CICS program. The spin operator $\hat{S}^2$, when operating on such determinants, will not generate any function outside the space. The space is "closed" under operations with $\hat{S}^2$, which will guarantee a CI expansion with correct spin symmetry. This property is used in the calculation of nuclear spin–spin coupling constants, as described later, where a correct triplet wave function is needed in the space spanned by (37)–(39) with a closed-shell reference state. For open-shell cases and when different orbitals for different spin are used, a wave function based on this type of expansion will not have the correct spin symmetry. This error can, however, be expected to be small in most cases. A rough idea of the accuracy of the determinantal expansion is obtained by noting that for equal orbitals for different spin the first-order interacting space (configurations interacting directly with the reference state) is included in the space spanned by all single and double replacements.

The length of the expansion is, in open-shell cases, about a factor of three longer than an expansion in projected first-order interacting CSFs, and of approximately the same length as an expansion in all projected configurations. An expansion in determinants with different orbitals for different spin is advantageous especially in those cases where a single RHF determinant is not a good representation of the wave function, as is usually the case when a molecule dissociates. An illustration of this for the HF molecule will be discussed later. The main disadvantage with different space orbitals is the increased number of molecular two-electron integrals. The list of such integrals will be four times longer, which makes the integral transformation *three* times slower, and the CI calculation *four* times slower. An efficient transformation program is consequently even more important for the CISD than for the CICS program. A modification of the CICS transformation to include the possibility of

different orbitals for different spin is included in the CISD package. The actual CI program has essentially the same general structure as has been described for the CICS case, including the index list and special routines for each integral type. With the restriction of paired spin-orbitals removed, the number of integral types has increased, and the program is correspondingly larger. The coupling coefficients will, however, simply be plus or minus one. This makes it possible to write the contributions to σ without reference to any coupling tables. We obtain the following contributions to σ from interactions between double-replacement determinants:

$$\Delta\sigma_{i_\mu j_\nu \to a_\mu b_\nu} = \sum_\kappa \sum_{c_\kappa} (-1)^p [f^\nu_{b_\nu c_\kappa} C_{i_\mu j_\nu \to a_\mu c_\kappa} \delta_{\kappa\nu} + f^\mu_{a_\mu c_\kappa} C_{i_\mu j_\nu \to c_\kappa b_\nu} \delta_{\kappa\mu}]$$

$$+ \sum_\kappa \sum_{k_\kappa} (-1)^{p+1} [f^\nu_{k_\kappa j_\nu} C_{i_\mu k_\kappa \to a_\mu b_\nu} \delta_{\kappa\nu} + f^\mu_{i_\mu k_\kappa} C_{k_\kappa j_\nu \to a_\mu b_\nu} \delta_{\kappa\mu}]$$

$$+ \sum_{k_\mu > l_\nu} [(i_\mu k_\mu | j_\nu l_\nu) - (i_\mu l_\nu | k_\mu j_\nu) \delta_{\mu\nu}] C_{k_\mu l_\nu \to a_\mu b_\nu}$$

$$+ \sum_{c_\mu > d_\nu} [(a_\mu c_\mu | b_\nu d_\nu) - (a_\mu d_\nu | c_\mu b_\nu) \delta_{\mu\nu}] C_{i_\mu j_\nu \to c_\mu d_\nu}$$

$$+ \sum_\kappa \sum_{k_\kappa c_\kappa} (-1)^p [(a_\mu i_\mu | c_\kappa k_\kappa) - (a_\mu c_\kappa | i_\mu k_\kappa) \delta_{\kappa\mu}] C_{k_\kappa j_\nu \to c_\kappa b_\nu}$$

$$+ \sum_\kappa \sum_{k_\kappa c_\kappa} (-1)^p [(b_\nu j_\nu | c_\kappa k_\kappa) - (b_\nu c_\kappa | j_\nu k_\kappa) \delta_{\kappa\nu}] C_{i_\mu k_\kappa \to a_\mu c_\kappa}$$

$$+ \sum_{k_\mu c_\nu} (-1)^p [(b_\nu i_\mu | c_\nu k_\mu) \delta_{\mu\nu} - (b_\nu c_\nu | i_\mu k_\mu)] C_{k_\mu j_\nu \to a_\mu c_\nu}$$

$$+ \sum_{k_\nu c_\mu} (-1)^p [(a_\mu j_\nu | c_\mu k_\nu) \delta_{\mu\nu} - (a_\mu c_\mu | j_\nu k_\nu)] C_{i_\mu k_\nu \to c_\mu b_\nu} \tag{40}$$

where i, j, and k denote internal spin-orbitals, a, b, and c denote external spin-orbitals, and the indices μ, ν, and κ denote spin α or β, so that f^ν is the α-spin Fock matrix if $\nu = \alpha$, or β-spin if $\nu = \beta$. p is the number of permutations necessary to line up equal spin-orbitals. For the interaction between single and double replacements we obtain

$$\Delta\sigma_{i_\mu j_\nu \to a_\mu b_\nu} = f^\nu_{b_\nu i_\nu} C_{i_\mu \to a_\mu} - f^\nu_{a_\mu j_\nu} C_{i_\mu \to b_\nu} \delta_{\mu\nu}$$

$$- f^\mu_{b_\nu i_\mu} C_{j_\nu \to a_\mu} \delta_{\mu\nu} + f^\mu_{a_\mu i_\mu} C_{j_\nu \to b_\nu}$$

$$+ \sum_{c_\mu} [(a_\mu c_\mu | b_\nu j_\nu) - (a_\mu j_\nu | c_\mu b_\nu) \delta_{\mu\nu}] C_{i_\mu \to c_\mu}$$

$$+ \sum_{c_\nu} [(a_\mu i_\mu | b_\nu c_\nu) - (c_\nu a_\mu | b_\nu i_\mu) \delta_{\mu\nu}] C_{j_\nu \to c_\nu}$$

$$+ \sum_{k_\nu} [(a_\mu j_\nu | i_\mu k_\nu) \delta_{\mu\nu} - (a_\mu i_\mu | j_\nu k_\nu)] C_{k_\nu \to b_\nu}$$

$$+ \sum_{k_\mu} [(b_\nu i_\mu | j_\nu k_\mu) \delta_{\mu\nu} - (b_\nu j_\nu | i_\mu k_\mu)] C_{k_\mu \to a_\mu} \tag{41}$$

Finally, for the interaction between single-replacement determinants the contributions are given by

$$\Delta\sigma_{i_\mu \to a_\mu} = \sum_{b_\mu} f^\mu_{a_\mu b_\mu} C_{i_\mu \to b_\mu} - \sum_{i_\mu} f^\mu_{i_\mu j_\mu} C_{j_\mu \to a_\mu}$$

$$+ \sum_\kappa \sum_{j_\kappa b_\kappa} [(a_\mu i_\mu | b_\kappa j_\kappa) - (a_\mu b_\kappa | i_\mu j_\kappa) \, \delta_{\kappa\mu}] C_{j_\kappa \to b_\kappa} \qquad (42)$$

The possibility to generalize the CISD method to cases with many reference determinants is in principle straightforward. A severe practical problem is the length of the expansion. A possible simplification would be to treat only the correlation between electrons with different spin. In the present scheme this corresponds to including only replacements of the $\alpha\beta$ type. Besides shortening the expansion, such a procedure also leads to a much shorter number of integral types and also to considerable simplifications in the formulas for the contributions to the σ vector. In spite of these simplifications an expansion of this type may be able to yield the major part of the structure-dependent correlation energy.

3.3. Complete CI Expansions

A particularly well-suited class of problems for the CIMI method is configuration interaction in the space of all possible spin- and space-allowed configurations, here denoted as complete CI. This type of wave function is of value in two quite different types of problems. It has been used as an investigating tool for problems where excited surfaces are of interest.[38,39] Usually it is appropriate in these cases to use a small basis set so that the Hamiltonian matrix can be diagonalized with conventional rotation methods like the Givens or Jacobi method. For this type of problem, with a short CI expansion, there is no advantage in using the CIMI method which does not yield a Hamiltonian matrix. The second type of problems where complete CI can be efficiently used is in accurate investigations on systems with few valence electrons. The CIMI methods has in these cases great advantages since it is relatively easy to set up the formulas for the calculation of the σ vector. For two valence electrons the CICS or CISD programs can be directly used. A special program (CI3) for the case of complete CI on three-electron systems has recently been constructed[40] and a similar four-electron program is presently being developed. Programs for complete CI on more than four electrons would probably not be so useful since the number of configurations soon becomes prohibitive.

The main reason for the relative simplicity in applying the CIMI method for complete CI problems is the small number of integral types which occur in

this case. Only the fourteen types of two-electron integrals given in Table 1 will appear in the equations determining the $\boldsymbol{\sigma}$ vector. The precise way in which one of these integral types is handled in the program is illustrated in Table 2. As mentioned in the section about the coupling coefficients, this description of the contributions to the $\boldsymbol{\sigma}$ vector is preferable from the programming point of view. The more compact description used for the CICS and the CISD programs is however possible to use also for the CI3 program, but the coupling tables will have a more complicated structure in this case.

For three electrons forming a doublet state, it is possible to write down three different types of configuration state functions. If two space orbitals are equal we get

$$\Phi_{aab} = [\varphi_a \bar{\varphi}_a \varphi_b] \tag{43a}$$

If all orbitals are different two linearly independent doublet state functions can be constructed:

$$\Phi_{abc}^{(1)} = \frac{1}{\sqrt{6}}\{2[\varphi_a \bar{\varphi}_b \varphi_c] - [\varphi_a \varphi_b \bar{\varphi}_c] - [\bar{\varphi}_a \varphi_b \varphi_c]\} \tag{43b}$$

$$\Phi_{abc}^{(2)} = \frac{1}{\sqrt{2}}\{[\varphi_a \varphi_b \bar{\varphi}_c] - [\bar{\varphi}_a \varphi_b \varphi_c]\} \tag{43c}$$

With these definitions for the CSFs a part of the general contribution to a σ element takes the form

$$\Delta \sigma_{abc} = \sum_{d \geq e} \{j_1(\mu, \nu)(bd|ce) + k_1(\mu, \nu)(be|cd)\}C_{ade}$$

$$+ \sum_{d \geq e} \{j_2(\mu, \nu)(ad|ce) + k_2(\mu, \nu)(ae|cd)\}C_{dbe}$$

$$+ \sum_{d \geq e} \{j_3(\mu, \nu)(ad|be) + k_3(\mu, \nu)(ae|bd)\}C_{dec} + \cdots \tag{44}$$

where contributions in terms of single sums have been omitted. The coupling coefficients j_i and k_i, which in this case depend on the permutation of indices $a-e$ in a more complicated way, are given in Table 6. To be able to set up the general expressions given in this table four parameters $(r, s, t,$ and $u)$ had to be introduced. This makes the usefulness of the table even more doubtful.

A fairly detailed timing analysis of the CI3 program has been made for a calculation on H_3.[40] It was found that the CPU time was shared roughly equal between index handling and the actual multiplications according to (4). As expected very little time was spent identifying and sending the integrals to the appropriate subroutines, and in the diagonalization routine once the σ vector had been constructed. The most efficient way to speed up a calculation on a particular system is to reduce the number of integrals that significantly contribute to the energy, as the time needed is directly proportional to the number of integrals. One way of doing this is to delete orbitals after a transformation to

Table 6. Coupling Coefficients for the Interaction Elements Defined in Eq. (44)[a]

μ	ν 1	ν 2	ν 3	μ	ν 1	ν 2	ν 3
	$j_1(\mu,\nu)$				$k_1(\mu,\nu)$		
1	-1	—	—	1	0	—	—
2	$(u\sqrt{\tfrac{3}{2}}+2)$	$(1-3r/2+rs)$	—	2	0	$(rs+3s/2-1)$	—
3	$(u\sqrt{\tfrac{1}{2}}+3)$	$r\sqrt{3}/2$	$(1-3r/2)$	3	$3-u\sqrt{2}$	$-s\sqrt{3}/2$	$(1-3s/2)$
	$j_2(\mu,\nu)$				$k_2(\mu,\nu)$		
1	$-u$	—	—	1	0	—	—
2	$\sqrt{\tfrac{3}{2}}$	$(1-r/2)$	—	2	$-\sqrt{\tfrac{3}{2}}$	$(r/2-1)$	—
3	$u\sqrt{\tfrac{1}{2}}$	$\sqrt{3}/2$	$(1-3r/2)$	3	$u\sqrt{\tfrac{1}{2}}$	$\sqrt{3}/2$	$(1-3r/2)$
	$j_3(\mu,\nu)$				$k_3(\mu,\nu)$		
1	0	—	—	1	0	—	—
2	$-u\sqrt{\tfrac{3}{2}}$	$(rs-3r/2+1)$	—	2	0	$(3s/2-1-rs)$	—
3	$u\sqrt{\tfrac{1}{2}}$	$-r\sqrt{3}/2$	$(1-3r/2)$	3	$3-u\sqrt{2}$	$s\sqrt{3}/2$	$(1-3s/2)$

[a] The indices (μ,ν) refer to the CSFs defined in (43a)–(43c). The parameters used are defined according to:

$$r = \begin{cases} 0 & \text{no permutation} \\ 1 & \text{otherwise} \end{cases} \qquad s = \begin{cases} 0 & \text{two permutations} \\ 1 & \text{otherwise} \end{cases}$$

$$t = \begin{cases} -1 & \text{index 2 and 3 permuted} \\ 0 & \text{no permutation} \\ 1 & \text{index 1 and 2 permuted} \end{cases} \qquad u = \begin{cases} -1 & d=e \\ 1 & \text{otherwise} \end{cases}$$

natural orbitals. Methods in which the number of small integrals can be directly maximized are of great interest but have not yet been investigated.

4. Examples of CI Calculations Performed with the CIMI Method

In this section we shall briefly discuss some CI studies in which the CIMI method has been applied. The discussion will be concentrated around the trends of the results and the reader is referred to the separate articles for more details.

The CIMI method has so far been applied to three different types of CI expansions; a closed-shell single-determinant reference state including all single- and double-replacement state functions (a CSSRS-expansion); a single determinant UHF reference state including all single- and double-replacement determinants without spin projection (an OSSRS-expansion), and finally complete CI expansion (including all CSFs obtainable from a given orbital set) for three-electron systems.

4.1. Studies on Closed-Shell Systems

The closed-shell version of the CIMI method has been implemented as the MOLECULE-CICS programs. Its main use is in calculations on molecules in their ground electronic states and on molecular interactions of moderate energy (e.g., hydrogen bond energies, etc.). Very weak van der Waals interactions require, however, a more accurate wave function, also including higher-order replacements, if results with an accuracy of a few degrees Kelvin are desired.

Apart from missing certain types of configurations, the accuracy of the wave function is determined by the length of the expansion, which for a given symmetry of the system under consideration, depends on the size of the orbital set. In applications with the CIMI method the limitations to this length are usually set by the dimension of the available processor storage and not so much by time requirements. It is necessary to have random access to two CI vectors [$\mathbf{C}^{(k)}$ and $\mathbf{C}^{(k-1)}$ in Eq. (10)] and the index vector simultaneously. Thus two floating point vectors and one integer vector have to be kept in the processor storage. The total storage requirements are determined by the number $2N_{CI} + N_{conf}$, where N_{CI} is the length of the expansion and N_{conf} is the number of *possible* configurations:

$$N_{conf} = \tfrac{1}{4}n_{int}(n_{int}+1)\,n_{ext}(n_{ext}+1) + n_{int} \cdot n_{ext}$$

where n_{int} and n_{ext} are the sizes of the internal and external orbital sets, respectively. A recent calculation on the water dimer had $n_{int} = 8$ and $n_{ext} = 58$. This gave $N_{conf} = 62,060$ and $N_{CI} = 56,268$. Approximately 1200 kbytes of IBM processor storage was used in this case. On the other hand, calculations with N_{CI} around 10,000 can be done with a storage size of less than 500 kbytes (the storage requirements can be reduced further if multiple passes over the integral list are allowed). Timing is another bottleneck in all types of CI calculations. The CIMI method minimizes the number of necessary multiplications needed to build the Hamiltonian matrix, as the coupling coefficients A in (4) can be factorized out of matrix elements of similar type. It is, however, necessary to construct the nonzero elements of the Hamiltonian matrix in every iteration. The total computation time will, therefore, be proportional to the number of iterations and it becomes important to use quickly convergent iteration procedures. Using the variation perturbation technique described earlier typically 6–8 iterations are necessary to converge to around 10^{-6} a.u. in the correltion energy for a closed-shell case with one dominant configuration. Figure 3 shows how the CPU time for one iteration in the MOLECULE-CICS program varies as a function of the number of CSFs. The I/O time is very short (CPU efficiency around 90% in typical cases) and significantly differs on this point from conventional CI methods. We conclude, on the basis of the data for core space and timing, that CIMI calculations with up to 10^4 CSFs require only a moderate amount of computer time and can be done with a limited core
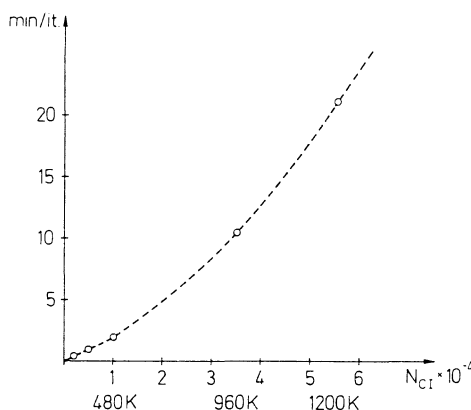
Fig. 3. Timing for the CICS program. The figure shows the CPU time for one iteration (computer: IBM 360/91) as a function of the number of configurations. Core storage requirements (in bytes) are also indicated.

space. On the large computers available today a CI expansion of 10^5 CSFs is possible and would not be prohibitively time consuming.

What accuracy can we expect to obtain with a CI expansion of the closed-shell type? One limitation is related to the incorrect dissociation behavior of the closed-shell determinant. At large internuclear separations several configurations have comparable weights and an ideal CI expansion would include single and double replacements with respect to all these configurations. The missing configurations corresponding to higher-order replacements can thus be expected to be strongly structure dependent. The possibility of using the CSSRS expansion in calculations of energy hypersurfaces is, therefore, restricted to cases which dissociate correctly in the HF approximation. This means essentially that only interactions between closed-shell systems can be studied. Calculations of portions of the energy hypersurfaces close to the equilibrium geometry should, however, be less affected by the limitation to a single reference state, since the additional configurations usually become important only at larger internuclear separations. Such calculations have been performed on a number of different molecules using a variety of Gaussian basis sets. Some of the results are collected in Table 7. The importance of an appropriate basis-set choice is clear from these results. Calculations not including polarization functions will, in general, not yield reliable equilibrium distances, as is illustrated by the calculations on H_2O and HF. These calculations were made with a basis set of essentially "double zeta" quality. Calculated distances improve considerably when polarization functions are added to this basis set and differ in all cases, except acetylene, less than 0.005 Å from the experimental values. This is very gratifying since very large basis sets cannot be used for other than small molecular systems. In general, we expect the single reference state approximation to give a better description of the near-equilibrium energy hypersurface for single bonded systems than for multiple bonds, as illustrated by the results on acetylene. The additional π bonds which are present in the latter case are usually weaker than the σ bond, and

Table 7. Equilibrium Geometries Obtained in CI Calculations Using a CSSRS Expansion

Molecule	Basis set[a]	Coordinate	SCF results[b]	CI results[c]	Observed	Reference
NH_3	$\langle N/4, 2, 1/H/3, 1\rangle$	$d(NH)$	1.004	1.016	1.012	
		$\sphericalangle HNH$	105.5°	102.5°	106.7°	46
H_sO	$\langle O/5, 3/H/2\rangle$	$d(OH)$	0.954	0.979	0.957	48
		$\sphericalangle (HOH)$	112.4°	112.4°	104.5°	
H_2O	$\langle O/5, 4, 1/H/3, 1\rangle$	$d(OH)$	0.944	0.960	0.957	
		$\sphericalangle HOH$	105.3°	103.8°	104.5°	43
H_3O^+	$\langle O/5, 4, 1/H/3, 1\rangle$	$d(OH)$	0.959	0.972	—	
		$\sphericalangle HOH$	113.5°	111.6°	—	43
HCN	$\langle N, C/6, 3, 1/H/3, 1\rangle$	$d(HC)$	1.063	1.068	1.066	
		$d(CN)$	1.137	1.153	1.153	49
CH_4	$\langle C/4, 2, 1/H/2, 1\rangle$	$d(CH)$	1.082	1.092	1.088	47
HF	$\langle F/4, 2/H/2, 1\rangle$	$d(FH)$	0.916	0.932	0.917	45
C_2H_2	$\langle C/4, 2, 1/H/2, 1\rangle$	$d(CC)$	—	1.211	1.207	
		$d(CH)$	—	1.074	1.061	50
C_2H_4	$\langle C/4, 2, 1/H/2, 1\rangle$	$d(CC)$	—	1.337	1.337	
		$d(CH)$	—	1.091	1.086	
		$\sphericalangle HCH$	—	117.2°	117.3°	50

[a] A basis set of contracted Gaussian functions is used in all cases. Only the contracted set is given.
[b] Distances in angströms.
[c] The expansion includes all single and double replacement CSFs, except from the core orbitals.

configurations containing antibonding molecular orbitals of π type can therefore be expected to have a larger weight than the corresponding σ-antibonding configurations. Higher-order replacement states, therefore, become more important in this case.

Another question is whether the results shown in Table 7 will persist if even larger basis sets are used. Some indication for this being the case is given by the results obtained by Meyer for the first and second row hydrides,[41] using extended basis sets. Errors in calculated equilibrium distances were in all cases found to be less than 0.005 Å. These results were obtained with the PNO–CI method, which is essentially parallel to the CSSRS expansion. Inclusion of higher-order replacements in an approximate way diminished the error to around 0.002 Å.

The large basis-set calculations of Meyer also gives an indication of how much correlation energy it is possible to obtain with a CSSRS expansion. Thus for H_2O 90% of the empirically estimated value was obtained,[42] which is probably close to the limiting value. Examples of correlation energies obtained with smaller basis sets on the ammonia molecule are given in Table 8. The importance of polarization functions is again clear. Less than 50% of the correlation energy is obtained, if they are not included. A CI expansion based on a "double zeta plus polarization" basis yields, on the other hand, around 70% of the valence electron correlation energy. Polarization functions describe angular correlation, which is an important and structure-dependent

part of the total correlation energy. The inclusion of such functions in the basis set is therefore essential if an accurate description of the chemical bond is desired. Further extensions of the basis set will only slowly improve the result.

Correlation effect on interaction energies between closed-shell systems are usually small in magnitude. Typical effects are induced dipole–dipole interactions (van der Waals interactions) and charge delocalization. The first effect increases the magnitude of the correlation energy and consequently increases the binding energy. The interaction energy is dominated by this term in the case of weakly interacting closed-shell molecules. The second effect usually leads to a decrease in magnitude of the correlation energy caused by the effective charge seen by the electrons. A typical example is H_3O^+. A recent calculation,[43] using the CSSRS expansion, predicted the correlation energy for this ion to be 1.5 kcal/mol smaller in magnitude than for the water molecule.

Changes in the intramolecular correlation energy can also give important contributions to the interaction energy between closed-shell systems. Such changes can be caused by polarization or by structural changes (e.g., changes in bond distances). CSSRS calculations on the water dimer give an illustration of the importance of polarization and dispersion effects on the binding energy. The correlation energy was found to increase the binding energy with 0.9 kcal/mol (from 5.14 to 6.05 kcal/mol), or 18% in this case.[43] A considerable shortening of the oxygen–oxygen bond from 2.99 to 2.92 Å was also observed (a linear hydrogen bond structure was assumed in these calculations). Strongly interacting systems ($\Delta E > 10$ kcal/mol) will in some cases undergo structural changes which in turn influence the correlation energy. The incorrect behavior of a closed-shell Hartree–Fock wave function at dissociation limits will, for example, give rise to appreciable correlation effects when bond distances are changed. The interaction between the ion OH^- and H_2O gives an illustration of this effect. This system has recently been studied both on the SCF and the CI level.[44] The SCF calculation of the equilibrium geometry of the system $[H_a-O_a-H_bO_bH_c]^-$ gave a value of 1.02 Å for the distance R (H_bO_b)

Table 8. Correlation Energy for NH_3 Obtained with a CSSRS Expansion for Different Basis Sets

Basis set[a]	Number of external orbitals	Number of CSFs	Correlation energy,[b] a.u.
⟨N/4, 2/H/2⟩	11	875	−0.1328
⟨N/5, 3/H/3⟩	17	2,271	−0.1424
⟨N/4, 2, 1/2, 1⟩	25	2,690	−0.1909[c]
⟨N/5, 3, 1/3, 1⟩	32	4,335	−0.2033[c]
⟨N/7, 6, 1/2, 1⟩	40	10.800	−0.2428

[a] Contracted Gaussian functions. The primitive basis set is (N/10, 6, 1/H/5, 1).
[b] Estimated exact value is −0.328 a.u.
[c] 1s core electrons frozen.

Table 9. Binding Energies for Some Closed-Shell Interacting Systems[a]

System	SCF	CI	Total[b]	Reference	Experimental
$H^+-OH_2^c$	174.3	172.8	167.5	43	166 ± 2
$Li^+-OH_2^c$	36.1	34.9	32.9	43	34.0
$F^--H_2O^c$	24.2	26.2	23.0	43	23.3
$H_2O-H_2O^c$	5.1	6.1	5.1	43	~5
$HO^--H_2O^c$	24.5	28.1	—	44	25
$HO^--H_2O^d$	34	39	—	45	25
F^--HF^d	53	56	—	45	37

[a] Units are kcal/mol.
[b] Including a correction for the change in zero-point vibrational energy.
[c] Basis set: $\langle O, F/5, 4, 1\rangle$, $\langle Li/5, 2\rangle$, $\langle H/3, 1\rangle$.
[d] Basis set: $\langle O, F/4,2\rangle$, $\langle H/2, 1\rangle$.

which is considerably longer than the value 0.94 Å obtained in an equivalent calculation on a free water molecule.[43] This is a considerable weakening of the $O_b H_b$ bond and we can expect that the correlation energy will lead to a further weakening, due to increasing near degeneracy effects leading to a larger hydrogen bond energy, an even longer distance $R(H_b O_b)$ and to a decrease in the proton transfer barrier. Such results were also obtained on the CI level. Thus $R(H_b O_b)$ was computed to be 1.08 Å. The binding energy which on the SCF level of approximation was calculated to be 24.5 kcal/mol, increased to 28.1 kcal/mol when correlation energy was taken into account. The proton transfer barrier simultaneously decreased from 1.4 to 0.2 kcal/mol.

A compilation of some calculated values for interaction energies between closed-shell systems is given in Table 9. The results obtained for $H_3O_2^-$ and FHF^- with the smaller basis set (essentially "double zeta") illustrate the importance of choosing an appropriate basis set for calculations of this type. Diffuse functions have to be used in order to obtain an adequate description of the negative ions F^- and OH^-. If such basis functions are not added an excessively large binding energy will be obtained.

4.2. Calculations Based on Expansion in Single Determinants

An important advantage with the OSSRS expansion as compared to the CSSRS expansion is the higher flexibility of the reference state which is introduced by allowing different space orbitals for different spins. With this type of expansion it becomes possible to use the CIMI method for studies of open-shell systems like radicals, etc. A part of the energy surface for the reaction $H + H_2O$ has recently been studied with the CISD program.[48] It is, however, also possible to use this method for closed-shell systems in cases where the RHF approximation corresponds to a saddle point instead of a true

minimum. This will, for example, occur in dissociation processes. To illustrate the usefulness of the OSSRS expansion in this case we have carried out a set of comparative calculations on the HF molecule. The atomic basis set used consisted of $11s$, $6p$, and $1d$ Gaussian functions contracted to $5s$, $3p$, and $1d$ for fluorine and a $5s$, $1p$ set contracted to $3s1p$ for hydrogen.[53] The fluorine d exponent was chosen to be 1.1 and the hydrogen p exponent to be 0.7, which is optimal for H_2. The results of these calculations are illustrated in Fig. 4, which shows the dissociation curve in four different approximations. The two upper curves have been obtained in the restricted (RHF) and the unrestricted (UHF) Hartree–Fock approximations. The different space orbitals give enough flexibility to allow the UHF curve to dissociate properly into a hydrogen atom and a spin-polarized fluorine atom. The characteristic breakdown of the RHF
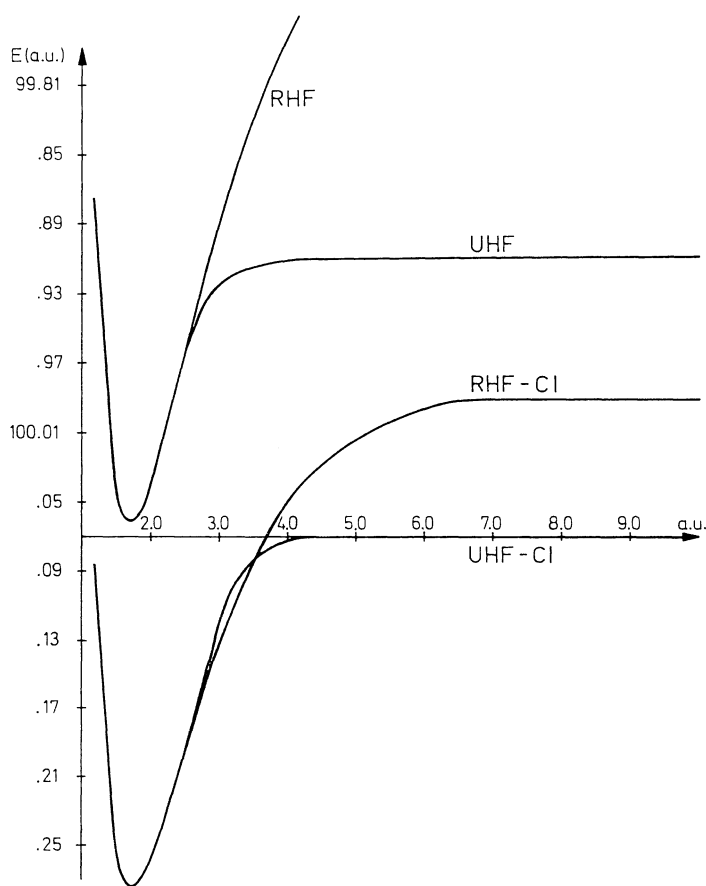
Fig. 4. Potential curves for HF calculated with the restricted (RHF) and unrestricted (UHF) methods and with CI expansions based on either an RHF or an UHF reference state (energies in atomic units).

approximation starts occurring at around 1.35 Å, corresponding to an energy of about 2.7 eV above the energy minimum, which occurs at a bond distance of 0.90 Å. The lowest vibrational frequencies will thus not be affected by the erratic behavior of the RHF curve. Outside 1.35 Å, the UHF solution yields more and more localized orbitals whereas the RHF orbitals remain delocalized. This is the usual behavior of the RHF solution. In fact very few systems dissociate to well-defined species in the RHF approximation. The system $H^+ + F^-$ represents a self-consistent solution to the RHF equations, but there also exists a solution which corresponds to a mixture of different ionic states and which has a lower energy. This solution is closely related to the first of the two closed-shell determinants which are needed for a proper description of the dissociated system.

The two lower curves in Fig. 4 are obtained from calculations with all single and double replacements out of the RHF and UHF determinants, respectively. Although somewhat surprising, the incorrect dissociation of the RHF approximation still persists in the RHF–CI curve, in spite of the fact that the two configurations needed for correct dissociation of a delocalized bond are included in the CSSRS expansion. The hydrogen molecule obviously dissociates correctly in the CSSRS approximation. We can use first-order perturbation theory in order to obtain a qualitative understanding of the RHF–CI curve in Fig. 4. A qualitatively correct potential curve for a single bonded system like HF is obtained with a two-configurational wave function of the type

$$\Phi_0 = C^I[\sigma\sigma] + C^{II}[\sigma^*\sigma^*] = C^I\Phi^I + C^{II}\Phi^{II} \tag{45}$$

where σ is the bonding and σ^* the corresponding antibonding molecular orbital (leaving out all equal orbitals). At infinite distances the coefficients take the values $C^I = -C^{II} = 1/\sqrt{2}$ and the wave function (45) then becomes equivalent to a localized description with one of the electrons on H and the other on F. In order to describe the correlation of the remaining electrons, all single- and double-replacement CSFs with respect to the two reference configurations should be added. Concentrating on the most important double replacements we can write the resulting wave function (at infinite HF distance) as

$$\Psi = \frac{1}{\sqrt{2}}(\Phi^I - \Phi^{II}) + \sum_{ij,ab} C^I_{ij\to ab}\Phi^I_{ij\to ab} + \sum_{ij,ab} C^{II}_{ij\to ab}\Phi^{II}_{ij\to ab}$$

where $\Phi^I_{ij\to ab}$ and $\Phi^{II}_{ij\to ab}$ denotes double-replacement states with respect to Φ^I and Φ^{II}. Since

$$\langle\Phi_0|\hat{H}|\Phi^I_{ij\to ab}\rangle = \langle\Phi_0|\hat{H}|\Phi^{II}_{ij\to ab}\rangle$$

we obtain, to first order in perturbation theory,

$$C^I_{ij\to ab} = C^{II}_{ij\to ab} = C_{ij\to ab}$$

Notice that Φ^I and Φ^{II} as well as the corresponding pairs of replacement states become degenerate at infinity. The total energy, to second order, is given by

$$E = \langle\Phi_0|H|\Psi\rangle = E_0 + 2 \sum_{ij,ab} C^I_{ij\to ab}\langle\Phi_0|H|\Phi^I_{ij\to ab}\rangle = E_0 + E_{corr} \qquad (47)$$

where the second term represents the correlation energy. It is clear from this expression that a CI expansion of the CSSRS type with double replacements form Φ^I only, will give an energy of $E_0 + \frac{1}{2}E_{corr}$. This is nicely illustrated in Fig. 4 where the RHF–CI curve approaches the midpoint between the UHF and UHF–CI curve when the distance becomes infinite.

In conclusion, the RHF–CI approach seems, in general, to be valid only in a region less than 0.5 Å away from the equilibrium distance, whereas the UHF–CI method seems to be able to generate quite useful potential curves for chemical reactions. The calculation on HF presented here thus yields an equilibrium r_e value of 0.92 Å and a dissociation energy $D_e = 5.6$ eV. The experimental values are 0.917 Å and 6.1 eV. On the UHF level these quantities were calculated to be 0.90 Å and 4.1 eV. Experimentally, the difference in correlation energy between F and HF can be estimated to 1.6 eV. Most of this structure-dependent part of the correlation energy is thus recovered in the UHF–CI calculation.

4.3. Three-Electron Complete CI Calculations

A recent study of the full potential surface for the H_3 system [19] will serve as an example of a calculation made with the CI3 program. This calculation is also illustrative of the type of reasoning which lies behind the final choice of the one-and many-particle basis sets.

The energy surface for linear H_3 had earlier been computed to high accuracy,[54] The absolute errors in the energies computed in this study were smaller than 1 kcal/mole with a much higher relative accuracy. The purpose of the CI3 calculations was to also predict the nonlinear part of the surface to a similar relative accuracy, with a reasonable effort in terms of computer time. The one-particle basis used for the linear case consisted of four s-, three p-, and two d-type functions of Slater type. For the nonlinear system, contracted Gaussian functions, CGTOs, were chosen since the integral evaluation is much more efficient for such functions with the computer programs presently available.

Comparative calculations on the hydrogen molecule with several different basis sets were made, in order to investigate possible truncations which could be made without any significant loss of accuracy. Deletion of one set of p functions (two instead of three) was found to cause a loss of accuracy in the (numerically computed) vibrational frequencies of the order of 10 cm^{-1}. The

corresponding change obtained with one set of d functions deleted was around 1 cm^{-1} This was considered more acceptable and four s-, three p-, and one d-type CGTOs were consequently chosen as the one-particle basis set.

The first step in a determination of an appropriate many-particle basis was to investigate the possibility of deleting molecular orbitals. For this purpose approximate natural orbitals were determined, both by perturbation theory and from a limited CI expansion. The latter orbitals were found to be slightly superior. Truncations in this orbital basis were made by only keeping orbitals with occupation numbers larger than specified thresholds. Test calculations at the transition state of H_3 led to a final choice of $30a'$ and $13a''$ orbitals. Complete CI calculations were then made in this space, using the CI3 program. Several points along the minimal energy path (which is linear) were calculated in order to finally check the validity of the truncations against the larger STO calculations. The two sets of calculations give minimal energy paths which are parallel to around 0.01 kcal/mole in a region of at least two atomic units around the barrier.

The timing (CPU time on an IBM 360/195) for each step of the calculation on a representative nonlinear point on the energy surface is as follows:

1.	Integral evaluation	5.72 min
2.	SCF calculation	3.48 min
3.	Full transformation	7.78 min
4.	Limited CI	5.37 min
5.	Truncated transformation	4.52 min
6.	Complete CI	19.45 min

This adds up to a total time of 46.32 minutes for each point on the surface. Around one hundred points had to be calculated in order to uniquely define the most important part of the surface. A detailed discussion of the results obtained in this study of H_3 will be presented elsewhere,[19] The CI3 program has also been used for studies of the reaction $H + Li_2$.[55]

4.4. Second-Order Properties

Experimentally, molecules are studied by observing their response to external perturbations, for example, electric and magnetic fields. The properties of a molecule are divided into classes according to which order of perturbation theory the corresponding operator will make a contribution to the energy. First-order properties are consequently calculated simply by taking the expectation value of the operator over the undisturbed wave function. For a one-electron operator h, as the dipole moment, this is achieved by a direct multiplication of the first-order density matrix D_{pq} and the corresponding

one-electron integral matrix J_{pq} in the same basis

$$\langle h \rangle = \sum_{p,q} D_{pq} I_{pq} \tag{48}$$

For a first-order N-electron property the corresponding procedure will require the Nth order reduced density matrix, and is consequently much more difficult to set up. The second-order properties are hard to calculate for another reason. They will, by definition, require the calculation of a disturbed wave function. Such a calculation will, in general, be as complicated as the calculation of the correlated wave function itself. The first-order wave function is, according to (8), defined through the differential equation

$$(\hat{H}_0 - E_0)|\psi^{(1)}\rangle = (E_1 - \hat{V})|\psi^{(0)}\rangle \tag{49}$$

By the usual expansion of $|\psi^{(0)}\rangle$ and $|\psi^{(1)}\rangle$ in a configuration basis

$$|\psi^{(0)}\rangle = \sum_k C_k^{(0)}|\Phi_k\rangle$$

$$|\psi^{(1)}\rangle = \sum_l C_l^{(1)}|\Phi_l'\rangle \tag{50}$$

where $|\Phi_l'\rangle$ is orthogonalized to $|\psi^{(0)}\rangle$ by

$$|\Phi_l'\rangle = (1 - \hat{P})|\Phi_l\rangle \tag{51}$$

with $\hat{P} = |\psi^{(0)}\rangle\langle\psi^{(0)}|$, and multiplying from the left by $\langle\Phi_m'|$ we transform the differential equation to an inhomogeneous equation system

$$\sum_l C_l^{(1)}[\langle\Phi_m'|\hat{H}_o|\Phi_l'\rangle - E_o(\delta_{lm} - C_l^{(0)}C_m^{(0)})] = -\langle\Phi_m'|\hat{V}|\psi^{(0)}\rangle \tag{52}$$

The correlated undisturbed wave function $|\psi^{(0)}\rangle$ will be an exact eigenfunction to $\hat{H}_0$ with the correlated energy as the eigenvalue if we define

$$\hat{H}_0 = \hat{P}\hat{H}\hat{P} + (1 - \hat{P})\hat{H}(1 - \hat{P}) \tag{53}$$

with the projection operator $\hat{P}$ defined as above. $\hat{H}$ is the undisturbed total Hamiltonian. The matrix elements of $\hat{H}_0$ in the basis $|\Phi'\rangle$ are related to the matrix elements of the undisturbed Hamiltonian $\hat{H}$ in the basis $|\Phi\rangle$ by

$$\langle\Phi_m'|\hat{H}_0|\Phi_l'\rangle = \langle\Phi_m'|\hat{H}|\Phi_l'\rangle = \langle\Phi_m|\hat{H}|\Phi_l\rangle - E_0 C_l^{(0)} C_m^{(0)} \tag{54}$$

The perturbation operator $\hat{V}$ contains besides the real perturbation $\hat{v}$ the additional terms of $\hat{H}$ not included in $\hat{H}_0$ so that

$$\hat{V} = \hat{P}\hat{H} + \hat{H}\hat{P} - 2\hat{P}\hat{H}\hat{P} + \hat{v} \tag{55}$$

The first three operators on the right-hand side will, however, not have any matrix elements between the basis sets $|\Phi'\rangle$ and $|\Phi\rangle$. The equation system will

therefore take the simple form

$$\sum_l C_l^{(1)}[\langle\Phi_m|\hat{H}|\Phi_l\rangle - E_0\,\delta_{lm}] = -\sum_k C_k^{(0)}[\langle\Phi_m|\hat{v}|\Phi_k\rangle - E_1\delta_{km}] \qquad (56)$$

The same equation system would have been obtained without the orthogonalization (27), which shows that $\psi^{(1)}$ is not entirely unique. The desired property, however, is defined through the second-order energy contribution, which for both basis sets is given by

$$E_2 = \sum_k \sum_l C_k^{(0)} C_l^{(1)}(\langle\Phi_k|\hat{v}|\Phi_l\rangle - E_1\,\delta_{kl}) \qquad (57)$$

where $|\psi^{(0)}\rangle$ is assumed as normalized.

The set of equations (56) can be solved by similar iteration schemes as were described in the section diagonalization procedures. Computationally, solving (56) again basically means construction of a vector $\sigma^{(k)}$ in iteration k, according to (3), and is therefore well suited to be handled by the CIMI method. The vector σ, however, has to be modified by the terms on the right-hand side, which depends on the pertubation operator but not on the undetermined coefficients $C_l^{(1)}$. These terms can be computed once and for all in the beginning of the calculation and stored.

The procedure described above has been used for the calculation of the nuclear spin–spin coupling constants observed in the splitting of NMR lines. Three different physical effects are responsible for this splitting: the electron orbital effect, the dipolar interaction between the electron and nuclear spin, and the Fermi contact interaction. For coupling between protons the latter effect is strongly dominant and is described by the operator

$$\hat{v} = \frac{16\pi\beta\hbar}{3}\sum_N \gamma_N \sum_k \delta(r_{kN})\hat{S}_k \cdot \hat{I}_N \qquad (58)$$

where $\delta(r_{kN})$ is the Dirac delta function at nucleus N, $\hat{S}_k$ denotes the spin of electron k, and $\hat{I}_N$ the spin of nucleus N. The nuclear spin–spin coupling appears in the second-order energy as a contribution of the type

$$E'_{NN} = hJ'_{NN}\hat{I}_N \cdot \hat{I}'_N \qquad (59)$$

where J'_{NN} is called the coupling constant between nucleus N and N'. The operator $\hat{v}$, according to (58), couples the singlet wave function $|\psi^{(0)}\rangle$ to triplet configurations $|\Phi'_m\rangle$, according to (52), which will require matrix elements of the undisturbed Hamiltonian over triplet configurations. As the MOLECULE-CICS program is restricted to singlet CSFs the CISD program has to be used. This program, however, has no explicit spin projection, but will automatically yield a correct triplet configuration in the space used. This means that for a double replacement from a closed-shell reference state we have to use all *six* possible determinants in order to obtain $|\psi^{(1)}\rangle$ as a true spin eigenfunction.

The CIMI method for nuclear spin–spin coupling has been applied to some smaller molecules. The calculation on H_2[57] with extended basis sets has an accuracy of a few percent for the coupling constant and is illustrative of the accuracy that can be obtained with this approach. For the H_2O molecule fairly nice agreement with experiments was also reached, whereas the results for NH_3, CH_4, C_2H_4, and C_2H_4 were more disappointing.[58] The difficulty in describing the cusp of the wave function at the nuclear center with Gaussian functions seems to be reponsible for this problem. Various ways of obtaining a better stability of the electron density at the nuclei are now being investigated. One way might be the use of Slater functions which have the right cusp behavior.

5. Concluding Remarks

We have, in this contribution, discussed in some detail the characteristics of the direct configuration interaction method. The merits of this method lie primarily in the possibility to use very long CI expansions, and thus obtain very accurate wave functions. The method is most easily adapted in the case of a single-determinant reference state including the full first-order subspace in the CI expansion. Examples have been given with a RHF and UHF reference state, where it has been shown that the direct method leads to very efficient algorithms for the determination of the CI coefficients.

The main drawback of the method is the lack of generality. It is not possible today to see how it could be generalized to arbitrary open-shell cases and to a more general selection of configurations. Special and very useful extensions are, however, possible. One rather straightforward way to generalize the method is to allow the reference state to be a linear combination of closed-shell determinants and include the first-order subspace with respect to all these determinants. Such a wave function gives a correct description of singlet states in which the electrons can be pairwise coupled to singlets. It then becomes possible to treat properly, for example, dissociation of single bonds and excited singlet states. Also the case of one odd electron outside a closed shell can be treated by means of a virtual coupling to a noninteracting electron. A computer program which can use this more general type of CI expansion is presently being developed. Future work on the CIMI method will also be related to the problem of including open-shell configurations in the reference state.

References

1. S. F. Boys, Electronic wave functions, I. A general method of calculation for the stationary states of any molecular system, *Proc. R. Soc. London, Ser. A* **200**, 542–554 (1950).

2. S. F. Boys, Electronic wave functions. II. A calculation for the ground state of the beryllium atom, *Proc. R. Soc. London, Ser. A* **201**, 125–137 (1950).

3. D. R. Hartree, W. Hartree, and B. Swirles, Self-consistent field, including exchange and superposition of configurations with some results for oxygen, *Philos. Trans. R. Soc. London, Ser. A* **238**, 229–247 (1939).

4. E. A. Hylleraas, Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium, *Z. Phys.* **54**, 347–366 (1929).

5. A. P. Jucys, On the Hartree–Fock method in multi-configuration approximation, *Adv. Chem. Phys.* **14**, 191–206 (1969) (atoms).

6. G. Das and A. C. Wahl, Extended Hartree–Fock wavefunctions: Optimized valence configurations for H_2 and Li_2, optimized double configurations for F_2, *J. Chem. Phys.* **44**, 87–96 (1966) (diatomic molecules).

7. T. L. Gilbert, Multiconfigurational self-consistent-field theory for localized orbitals. I. The orbital equation, *Phys. Rev. A* **6**, 580–600 (1972). A thorough discussion of the subject can also be found in Ref. 30.

8. B. Roos, A new method for large scale CI calculations, *Chem. Phys. Lett.* **15**, 153 (1972).

9. B. Roos and P. Siegbahn, in: *Chemical and Biochemical Reactivity*, *the Jerusalem Symposia on Quantum Chemistry and Biochemistry*, VI, The Israel Academy of Sciences and Humanities, Jerusalem (1974).

10. J. Almlöf, B. Roos, and P. Siegbahn, the Program System MOLECULE, Reference Manual (to be published).

11. J. K. L. MacDonald, Successive approximations by the Rayleigh–Ritz variation method, *Phys. Rev.* **43**, 830–833 (1933).

12. H. J. Silverstone and O. Sinanoğlu, Many-electron theory of nonclosed-shell atoms and molecules. I. Orbital wave function and perturbation theory, *J. Chem. Phys.* **44**, 1899–1907 (1966); II. Variational theory, *J. Chem. Phys.* **44**, 3608–3617 (1966).

13. P.-O. Löwdin, Quantum theory of many-particle systems. I. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction, *Phys. Rev.* **97**, 1474–1489 (1955).

14. A. J. Coleman, Structure of fermion density matrices, *Rev. Mod. Phys.* **35**, 668–689 (1963).

15. A. D. McLean and B. Liu, Classification of configurations and the determination of interacting and noninteracting spaces in configuration interaction, *J. Chem. Phys.* **58**, 1066–1078 (1973).

16. O. Sinanoğlu, Many-electron theory of atoms and molecules. I. Shells, electron pairs versus many-electron correlations, *J. Chem. Phys.* **36**, 706 (1962).

17. W. Meyer, PNO–CI studies of electron correlation effects. I. Configuration expansion by means of nonorthogonal orbitals, and application to the ground state and ionized states of methane, *J. Chem. Phys.* **58**, 1017–1035 (1973).

18. R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics*, Academic Press, London (1969).

19. B. Liu and P. Siegbahn, An accurate three-dimensional potential surface for H_3, to be published.

20. C. Bender, private communication.

21. R. K. Nesbet, Algorithm for diagonalization of large matrices, *J. Chem. Phys.* **43**, 311–312 (1965).

22. I. Shavitt, C. F. Bender, A. Pipano, and R. P. Hosteny, The iterative calculation of several of the lowest or highest eigenvalues and corresponding eigenvectors of very large symmetric matrices, *J. Comput. Phys.* **11**, 90–108 (1973).

23. P.-O. Löwdin, Studies in perturbation theory IX. Upper bounds to energy eigenvalues in Schrödinger's perturbation theory, *J. Math. Phys.* **6**, 1341–1353 (1965).

24. E. Brändas and O. Goscinski, Variation-perturbation expansions and Padé-approximants to the energy, *Phys. Rev. A* **1**, 552–560 (1970).

25. O. Goscinski and E. Brändas, in: *Theory of Electronic Shells of Atoms and Molecules*, Report from the Vilnius International Symposium, 1969, Mintis, Vilnius (1971).

26. R. J. Bartlett and E. J. Brändas, Reduced partitioning procedure in configuration interaction studies. II. Excited states, *J. Chem. Phys.* **59**, 2032–2042 (1973).

27. E. R. Davidson, The iterative calculation of a few of the lowest eigenvalues and corresponding eigenvectors of large real-symmetric matrices, *J. Comput. Phys.* **17**, 87–94 (1975).

28. V. R. Saunders and I. H. Hillier, A "level-shifting" method for converging closed shell Hartree–Fock wave functions, *Int. J. Quantum Chem.* **7**, 699–705 (1973).

29. V. R. Saunders and M. F. Guest, in: *Proceedings of SRC Atlas Symposium No. 4, "Quantum Chemistry—the State of the Art"* (V. R. Saunders and J. Brown, eds.), Atlas Computer Laboratory, Chilton Didcot, Oxfordshire (1975).

30. J. Hinze, MC-SCF. I. The multi-configurational self-consistent-field method, *J. Chem. Phys.* **59**, 6424–6432 (1973).

31. P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine, in: *Wave Mechanics the First Fifty Years* (W. C. Price, S. S. Chissik, and T. Ravensdale, eds.), pp. 88–98, Butterworth & Co., London (1973).

32. C. Edminston and M. Krauss, Pseudonatural orbitals as a basis for the superposition of configurations. I. He_2^+, *J. Chem. Phys.* **45**, 1833–1839 (1966).

33. W. P. Reinhardt and J. D. Doll, Direct calculation of natural orbitals by many-body perturbation theory: Application to helium, *J. Chem. Phys.* **50**, 2767–2768 (1969).

34. P. Dejardin, E. Kochanski, A. Veillard, B. Roos, and P. Siegbahn, MC–SCF and CI calculations for the ammonia molecule, *J. Chem. Phys.* **59**, 5546–5553 (1973).

35. P. Bertoncini and A. C. Wahl, *Ab initio* calculation of the helium–helium $^1\Sigma_g^+$ potential at intermediate and large separations, *Phys. Rev. Lett.* **25**, 991–994 (1970).

36. H. F. Schaefer, D. R. McLaughlin, F. E. Harris, and B. J. Alder, Calculation of the attractive He pair potential, *Phys. Rev. Lett.* **25**, 988–990 (1970).

37. M. Yoshimine, The use of direct access devices in problems requiring the reordering of long data lists, IBM Corp. Tech. Rep. RJ 555 (1973).

38. F. E. Harris and H. H. Michels, Open-shell valence configuration-interaction studies of diatomic and polyatomic molecules, *Int. J. Quantum Chem.* **1S**, 329–338 (1967).

39. H. F. Schaefer and F. E. Harris, *Ab initio* calculations on 62 low-lying states of the O_2 molecule, *J. Chem. Phys.* **48**, 4946–4955 (1968).

40. P. Siegbahn. in: *Proceedings of SRC Atlas Symposium No. 4, "Quantum Chemistry—the State of the Art"* (V. R. Saunders and J. Brown, eds.), Atlas Computer Laboratory, Chilton Didcot, Oxfordshire (1975).

41. W. Meyer, in: *Proceedings of SRC Atlas Symposium No. 4, "Quantum Chemistry—the State of the Art"* (V. R. Saunders and J. Brown, eds.), Atlas Computer Laboratory, Chilton Didcot, Oxfordshire (1975).

42. W. Meyer, Ionization energies of water from PNO–CI calculations, *Int. J. Quantum Chem.* **5S**, 341–348 (1971).

43. G. H. F. Diercksen, W. P. Kraemer, and B. Roos, SCF-CI Studies of correlation effects on hydrogen bonding and ion hydration, The systems: H_2O, $H^+ \cdot H_2O$, $Li^+ \cdot H_2O$, $F^- \cdot H_2O$ and $H_2O \cdot H_2O$, *Theor. Chim. Acta* **36**, 249–274 (1975).

44. G. H. F. Diercksen, W. P. Kraemer, and B. Roos, SCF-CI studies of the equilibrium structure and proton transfer barrier in $H_3O_2^-$, *Theor. Chim. Acta* **42**, 77–82 (1976).

45. A. Støgård, A. Strich, J. Almlöf, and B. Roos, Correlation effects on hydrogen-bond potentials. SCF-CI calculations for the systems HF_2^- and $H_3O_2^-$, *Chem. Phys.* **8**, 405–411 (1975).

46. J. Kowalewski and B. Roos, Large configuration interaction calculations of nuclear spin–spin coupling constants. III. Vibrational effects in ammonia, *Chem. Phys.* **11**, 123–128 (1975).

47. K. Niblaeus, private communication.

48. K. Niblaeus, B. Roos, and P. Siegbahn, An UHF-CI study of the H_3O radical, to be published.

49. P. K. Pearson, G. L. Blackman, H. F. Schaefer III, B. Roos, and U. Wahlgren, HNC molecule in interstellar space? Some pertinent theoretical calculations, *Astrophys. J.* **184**, L19–L22 (1973).

50. A. D. McLean and P. Siegbahn, to be published.

51. R. F. Hausman, Jr., S. D. Bloom, and C. F. Bender, A new technique for describing the electronic states of atoms and molecules—the vector method, *Chem. Phys. Lett.* **32**, 483–488 (1975).
52. The original tables published in Ref. 8 were unfortunately incorrect. The authors are grateful to Dr. N. C. Handy for pointing out a number of these errors.
53. F. B. van Duijneveldt, Gaussian basis sets for the atoms H–Ne for use in molecular calculations, IBM Research Report RJ 945 (1971).
54. B. Liu, *Ab initio* potential energy surface for linear H_3, *J. Chem. Phys.* **58**, 1925–1937 (1973).
55. P. Siegbahn and H. F. Schaefer III, Potential energy surface for $H + Li_2 \rightarrow LiH + Li$. I. Ground state surface from large scale configuration interaction, *J. Chem. Phys.* **62**, 3488–3495 (1975).
56. B. Liu and A. D. McLean, Accurate calculation of the attractive interaction of two ground state helium atoms, *J. Chem. Phys.* **59**, 4557–4558 (1973).
57. J. Kowalewski, B. Roos, P. Siegbahn, and R. Vestin, Large configuration interaction calculations of nuclear spin–spin coupling constants. I. HD molecule, *Chem. Phys.* **3**, 70–77 (1974).
58. J. Kowalewski, B. Roos, P. Siegbahn, and R. Vestin. Large configuration interaction calculations of nuclear spin–spin coupling constants. II. Some polyatomic molecules, *Chem. Phys.* **9**, 29–39 (1975).