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Individualized Configuration Selection in CI Calculations with Subsequent Energy Extrapolation

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A configuration selection method for CI calculations is discussed and applied in which the energy lowering produced in a secular equation by the addition of a given test species to a series of dominant configurations is used as an ordering parameter. Configurations with energy lowerings below a given energy cut-off value are not included in the final secular equations but instead a method of estimating the combined effect of the neglected species on the corresponding non-selected CI results is developed. The influence of the choice of main configurations used in the selection process is given close examination as well as the importance of the MO basis employed in the treatment as a whole; in the latter case a non-iterative procedure for obtaining approximate natural orbitals for such calculations is suggested. The resulting configuration selection procedure is equally applicable to all types of electronic states in any nuclear geometry and the results of the associated CI calculations are seen to be essentially equivalent to a complete treatment in which all single- and double-excitation species with respect to a *series* of dominant configurations in a given state are included.

Key words: Configuration interaction – Selection of configurations – Transition energies – Electronic spectra

1. Introduction

At least for the present it appears that CI methods constitute the only truly feasible means of obtaining correlated wavefunctions and associated expectation values therefrom for systems of reasonable size, certainly for those of general interest in chemistry. Since the dimensions of a *full* CI increase in a factorial manner with basis set size, there has never been much doubt that a straightforward approach to the attainment of multi-configuration wave-functions by this route is completely impractical for all but the smallest molecular systems; in order to achieve some appreciation of the futility in carrying the CI method to its theoretical limit on any kind of a suitable general scale one need only recall, for example, that recent attempts to adequately describe the molecular structure of such a relatively small molecule as ammonia [1] have employed basis sets containing up to 56 contracted gaussians.

As a result it becomes necessary in the design of CI treatments on a practical level to be quite selective in choosing configurations which are to be given explicit consideration in a given secular equation, with the seemingly well-founded hope that deletion of many of the more weakly interacting species,

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especially when treated in a systematic manner, will not greatly alter the overall results of the calculation relative to what would be obtained if the *full* CI were actually carried out. In addition the emphasis in such limited CI calculations need not be upon the attainment of all or even a large part of the total correlation energy but rather on the much more accessible goal of achieving a balance in the correlation effects for different electronic states of the same system, or for different nuclear conformations of the same state, thereby allowing for the accurate prediction of corresponding transition energies and/or related potential surfaces. The present paper discusses various approaches to the problem of selecting configurations and reports the results of one such method of general applicability which appears to have considerable promise in achieving the goals mentioned above.

2. Methods of Configuration Selection

Generally speaking the primary objective of any configuration selection procedure is to draw a clear and hopefully quantitative distinction between those configurations which make an important contribution to the total electronic wavefunction and those which do not. At the same time a second and perhaps equally important goal presents itself, namely to obtain an accurate prediction of any errors which occur in omitting the configurations rejected in the selection process, particularly to be able to *reliably estimate the energy contribution for the neglected species.*

Simple arguments based on perturbation theory suggest that a selection criterion which considers only the diagonal energies of a given configuration is not adequate. Off-diagonal Hamiltonian matrix elements between a given test configuration and one or more dominant species in the wavefunction of interest are also important for gauging its contribution to the total CI energy and thus some reasonably accurate estimate of the mixing coefficient of the test configuration in the full CI expansion is required in order to decide whether it should be included in the final CI or not. This observation by itself of course is by no means sufficient to completely specify the most effective procedure for accomplishing the desired selection, with one of the major questions remaining being whether to test the configurations individually or in large groups.

In both of the latter cases a subset of dominant or main configurations $\{\phi_m\}$ (which are the components of the zero-order wavefunction ψ_0) must be designated which forms the basis for the selection of the remaining species. All Hamiltonian matrix elements between these dominant species and each of the test configurations are then calculated while most and often all of those matrix elements connecting the different test species themselves are neglected. In *individualized* selection procedures this information is used piecemeal to evaluate separately the influence of each of the test configurations one after the other, that is, through a series of small calculations. On the other hand the *group* selection techniques, as exemplified by the so-called B_k approximation of Shavitt [2], employ a *single large calculation* (at least in principle involving the same group of matrix elements) in order to test the configurations *en masse.* The success of either approach can obviously only be assessed on the basis of wide-ranging numerical experiments, but prior to considering such specific calculated results some details about the exact procedures at hand should be discussed with an eye toward accomplishing certain practical objectives which present themselves when CI techniques are applied to the solution of typical chemical problems.

2.1. *Details of the Individualized Selection Technique*

Because of its reliance on a large number of test calculations to estimate the influence of the various configurations, it is quite important from a practical point of view to employ a rather small expansion for ψ_0 in the individualized selection procedure, thereby making the initial choice of the component main configurations quite critical. This fact raises the rather obvious question of: a) how to choose the main configurations in the first place and b) how to gauge the effect of adding still more configurations to the initial set. The first of these questions is relatively easy to answer, since generally the most important configuration in the wavefunction is known from consideration of qualitative MO theory, and additional species can be chosen on the basis of the magnitudes of their coefficients in a relatively small CI, one based for example on a selection procedure which employs only the leading configuration as ψ_0.

In general it is definitely desirable to employ more than one main configuration in the selection process since the leading configuration in the CI wavefunction does not always play a constant role for all states and all geometries considered. Furthermore, in this way the class of configurations given explicit consideration can more justifiably be restricted to all single- and double-excitation species with respect to just the members of the $\{\phi_m\}$ subset, since the set so generated includes most of the important triple and higher excitation species (with respect to the leading configuration) which judging from experience cannot safely be neglected. As to when it becomes acceptable to stop adding configurations for the ψ_0 expansion, that is again a matter that requires more quantitative study and hence will be deferred until the following section.

Once the main configurations are chosen there are at least two criteria which can be used to judge the importance of the various test configurations: the lowering in energy produced by each test species relative to the value obtained from ψ_0 alone can be estimated on the basis of perturbation theory [3, 4] (generally taken through second order) or it can be obtained directly from solution of the corresponding secular equations [5]. The perturbation method of course has the advantage of involving less computation, but since the great majority of the arithmetic operations required in either case goes into the calculation of the matrix elements, the time saving introduced by foregoing the solution of the actual secular equations is deceptively small (particularly for the small secular equations envisioned in the individualized selection technique). On the other hand, although the additional effort that goes into the direct solution allows for the readjustment of the coefficients in the ψ_0 expansion for each test species, experience seems to indicate that the selection of configurations proceeds with essentially the same results in either case, i.e. the ordering of the test configurations according to the magnitudes of the energy lowerings they produce is quite similar in the two methods. In the present work the appropriate secular equations are actually solved, mainly for the purpose of achieving the second major goal of the selection process, namely to obtain an accurate prediction of the total energy contribution of the configurations *not* chosen for the final CI calculation itself; for it appears that the actual energy lowerings produced in the test secular equations can be of significant utility for this purpose (*vide* Section 2.3).

This method can also easily be applied if more than one root of the same symmetry type is required in the CI. It is only necessary to insure that the set of main configurations is sufficiently large to allow for a realistic representation of all states of interest, not just that of lowest energy. The desired number of roots is then obtained from each of the secular equations involving $\{\phi_m\}$ and the test configuration, and the energy lowerings produced by the latter are then computed separately for each of the roots. In this case the maximal energy lowering for all the roots is compared with some cut-off value for the purpose of determining whether the test species should be included in the final CI. Inevitably multiple-root selection leads to larger secular equations but this consequence is clearly fundamental in origin.

Besides the choice of the main configuration subset $\{\phi_m\}$ there are two other points of uncertainty which need to be considered: the first of these is clearly the magnitude of the energy cut-off or *threshold value* T to be used and its influence on the final results; the other concerns the importance of the MO *basis set* in determining the results of the selection and ultimately of the entire CI calculation. The effect of T can be judged by the dependence of the final CI energy (or other properties) upon this quantity; obviously the goal is to effectively eliminate T as a parameter in the final results by means of a reliable estimate or extrapolation of the energy as T approaches zero (Section 2.3 and Section 3). The choice of the MO basis becomes less critical, of course, the more effective the selection process is in approaching the results of the corresponding full CI. Thus the purpose of the selection procedure is not only to allow the use of the full complement of the valence MO's (and in certain cases those of the inner shells also) while holding the size of the resultant secular equations to manageable limits, but also to reduce the importance of the choice of orbital basis itself; this aspect of the method will be taken up in Section 3.

One final point concerns the manner in which configurations containing more than one multiplet (CF) of the desired symmetry are handled. One can add all the CF's at once and solve a single secular equation or consider them separately in a series of smaller calculations. In the latter case Bunge [6] has suggested a method of generating the CF's in such a manner that the effect of a given configuration is concentrated in as few of the individual components as possible. Particularly in calculations involving high symmetry the elimination of all but the most important CF's in such configurations can lead to a considerable reduction in the order of the final CI problems to be solved. In the present work, however, each test configuration is considered *in toto* and the selection is based on the mean energy lowering per multiplet in a given configuration. Alternatively the possibility of treating each CF of a test configuration separately (hence rejecting a portion of its CF's but not all in a given case) also appears to have promise, especially when a subsequent attempt is made to account for the energy contribution of all neglected species in the final CI; the latter approach has the advantage of allowing the use of identical expansion coefficients for all corresponding CF's in isomorphic configurations.

2.2. Comparison with Group Selection Methods

In principle one is faced with much the same questions in designing a group selection method as in the individualized technique. A set of main configurations must be assumed at the outset, all Hamiltonian matrix elements between members of this set and all test configurations must be computed in addition to the elements connecting the main configurations themselves; the importance of the choice of an energy cut-off and a set of valence MO's must similarly be assessed. In Shavitt's B_k approximation [2] all matrix elements between the test configurations are simply set to zero, and the resultant secular matrix is diagonalized by conventional techniques. The coefficients of the test species in the resultant CI expansion are then combined with their respective diagonal energies to produce the desired estimations of the interactive capabilities (again in the form of energy lowerings) of each of the test configurations.

In practice, however, the number of main configurations employed in such treatments has been larger than that envisioned in the individualized selection technique discussed in Section 2.1. In previous work, for example, Shavitt has chosen as his "primary subset" of main configurations the entire double-excitation space of the SCF wavefunction (220 CF's). Whether such a large set of main configurations is really needed in the B_k approximation can only be answered by numerical experimentation, but at least as far as current practice is concerned it appears that the individualized selection technique requires a smaller number of reference species (and thus a smaller number of matrix elements to be computed) than its counterpart which treats all configurations together. In any event the question is not really so much whether a group or individualized selection method is to be preferred but rather how large a set of main configurations is adequate *in either case* to accomplish the physical and chemical objectives sought in the CI calculations in the first place. It is this question then which is considered in detail in the numerical applications of the individualized selection technique reported in Section 3.

2.3. Extrapolation to $T=0$ in the Individualized Selection Method

Regardless of which type of selection procedure is used, an important goal is to be able to accurately estimate the effect of those configurations which are not included in the final CI. In the individualized selection method an obvious route toward this end involves the summation of all the energy lowerings of those species which do not meet the selection criterion (as represented by the energy cut-off value T). Davidson, for example, has suggested [4] that one compare the sum of the energy lowerings (as obtained by perturbation theory) of the neglected test species with the total energy change effected by the CI in order to get at least a semiquantitative estimate of the consequences of employing a non-zero T, especially at different nuclear geometries. If one uses the actual secular equation energy lowerings as suggested in the present work it is not difficult to show that an essentially quantitative method for extrapolating the CI results to $T=0$ can in fact be formulated.

This point can best be illustrated by dividing the total configuration set in the $T=0$ CI into three subsets $\{\phi_m\}$, $\{\phi_s\}$, and $\{\phi_r\}$ denoting main, selected and discarded (remaining) configurations respectively. The zero-order wavefunction ψ_0 and that obtained in the final truncated CI (for a given value of T) can then be defined as:

$$\psi_0 = \sum_m c_m^0 \phi_m, \quad \text{and} \tag{1}$$

$$\psi(T) = \sum_m c_m(T)\,\phi_m + \sum_s c_s(T)\,\phi_s \tag{2}$$

while in like manner the wavefunction $\psi \equiv \psi(0)$ for the $T=0$ CI is obtained as

$$\psi = \sum_m c_m(0)\,\phi_m + \sum_s c_s(0)\,\phi_s + \sum_r c_r(0)\,\phi_r\,. \tag{3}$$

By construction the ϕ_r are weakly interacting species (particularly when T is quite small and the set $\{\phi_m\}$ is sufficiently representative), i.e. the mixing coefficients c_m^0 of the main configurations are probably not greatly altered by the presence of a given ϕ_r in the secular problem. In addition the coefficient of ϕ_r itself is expected to be essentially the same in the test calculation (with wavefunction ψ_r) as it would be in the $T=0$ CI treatment itself; hence the approximation

$$\psi_r \approx (\psi_0 + c_r(0)\,\phi_r)\,N \tag{4}$$

should be fairly realistic (ψ_r is normalized). Likewise the assumption that each ϕ_r is so weakly interacting as to not alter the relative weighting of the ϕ_m and ϕ_s species relative to their values in $\psi(T)$ leads to

$$\psi \approx \left[\psi(T) + \sum_r c_r(0)\,\phi_r\right] N'\,. \tag{5}$$

Under these assumptions the energy lowering ΔE_r obtained by adding ϕ_r to the original set of main configurations ϕ_m can be written as:

$$\begin{aligned}\Delta E_r &= \langle\psi_r|H|\psi_r\rangle - \langle\psi_0|H|\psi_0\rangle\\ &\approx [\langle\psi_0|H|\psi_0\rangle + 2\,\mathrm{Re}\{c_r(0)\,\langle\psi_0|H|\phi_r\rangle\} + |c_r(0)|^2\,\langle\phi_r|H|\phi_r\rangle]\\ &\quad\cdot(1+|c_r(0)|^2)^{-1} - \langle\psi_0|H|\psi_0\rangle\\ &\approx 2\,\mathrm{Re}\{c_r(0)\,\langle\psi_0|H|\phi_r\rangle\} + |c_r(0)|^2\,\{\langle\phi_r|H|\phi_r\rangle - \langle\psi_0|H|\psi_0\rangle\}\,.\end{aligned} \tag{6}$$

Following Bunge [7] it is then possible to use the first-order perturbation theory estimate of $c_r(0)$ to simplify this equation further:

$$\Delta E_r \approx c_r(0)\,\langle\psi_0|H|\phi_r\rangle\,. \tag{6'}$$

Similarly the total energy $E \equiv E(0)$ of the $T=0$ CI is obtained [using Eq. (5)] as

$$E = \langle\psi|H|\psi\rangle \approx E(T) + \sum_r c_r(0)\,\langle\psi(T)|H|\phi_r\rangle\,. \tag{7}$$

Finally, if ψ_0 approximates $\psi(T)$ to a sufficiently good extent, the ΔE_r values of Eq. (6) can be safely substituted for the corresponding terms of the summation in Eq. (7), thereby yielding the result:[1]

$$E \approx E(T) + \sum_r \Delta E_r \,. \tag{8}$$

The hope is then that by employing a) a small enough value of T and b) a sufficiently representative set of main configurations $\{\phi_m\}$ it will be possible to use Eq. (8) to reliably predict the $T=0$ CI energy (whose calculation by direct methods would otherwise not be feasible). This result gives added meaning to some of the points mentioned in Section 2.1, namely the desirability of determining what values of T and what sets of main configurations are adequate to insure an effective selection procedure, both in terms of the accuracy of the final result and also the magnitude of the computations to be explicitly carried through.

3. Applications of the Individualized Selection Technique

3.1. *Dependence of* CI *Results on the Threshold Value*

Probably the first question of interest in examining the characteristics of CI calculations based on a configuration selection technique is the manner in which the total energy in such a treatment varies with the energy cut-off value T employed. The results of Tables 1a, b for CI calculations on butadiene, ethylene and O_2 give a representative cross-section of this type of data. On an absolute scale it is clear that the energy of a given state generally does very rather strongly with T, at least down to cut-off values of a few microhartress (μh). In ethylene, for example, the ground state energy is observed to change by 0.0035 hartree (or 0.1 eV) when T is varied from 40–20 μh. Below T values of 5 μh the neglected configurations of course have a much smaller potential contribution to E, but in most cases the orders of the secular equations which need to be solved for such relatively small thresholds are already prohibitively large. The dependence of other properties on T can also be judged from Table 2 on the basis of results for the CN molecule. Again non-negligible changes are observed in virtually all cases, although the dipole and quadrupole moment results are seen to be relatively stable, especially below 20 μh. Not surprisingly the dipole velocity matrix elements are seen to be relatively sensitive to the magnitude of T, particularly in comparison to their counterparts for the dipole length operator.

While the changes in *absolute* energies with T are inevitable, those in more *relative* quantities would appear to have a much better chance of being of negligible magnitude. In Table 1b, for example, it is seen that both the ${}^3\Sigma_g^- - {}^1\Delta_g$ energy differences ΔE and the binding energies of each of these states remain essentially constant as T is decreased, despite the fairly substantial changes observed on an absolute scale in each case. It is really in this area of calculating

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[1] An alternative way of arriving at Eq. (8) (without resorting to perturbation theory) follows upon a straightforward evaluation of E using Eq. (5):

$$E = \langle\psi|H|\psi\rangle \approx E(T) + 2\,\mathrm{Re}\Big\{\sum_r c_r(0)\,\langle\psi(T)|H|\phi_r\rangle\Big\} + \sum_r c_r(0)^2\,[\langle\phi_r|H|\phi_r\rangle - \langle\psi(T)|H|\psi(T)\rangle]\,.$$

Comparison of this expression with Eq. (6) also leads directly to Eq. (8) under the same assumption as before, namely that ψ_0 approximates $\psi(T)$ to a sufficiently good extent in the selection procedure undertaken.

Table 1a. Variation of the total CI energy $E(T)$ as a function of the threshold value T for t-butadiene and ethylene in their respective electronic ground states

t-Butadiene, ^1A_g		Ethylene, ^1A_g	
$T \times 10^{-6}$	$E(T)$[a]	$T \times 10^{-6}$	$E(T)$[a]
20	−154.91682 (144)	100	−78.16929 (283)
5	−154.91810 (179)	80	−78.17095 (312)
3	−154.91823 (219)	60	−78.17457 (366)
1	−154.91862 (262)	40	−78.17839 (454)
0.5	−154.91867 (292)	20	−78.18191 (597)
SCF = −154.8573 ^1A_g MO's, 4 Mains core[c] = 13 valence set[c] = 12, 50 AO's		SCF = −78.00087 ^1A_g NO's[b], 2 Mains core[c] = 2 valence set[c] = 26, 32 AO's 2×2 CI = −78.03038 $c_1/c_2 = 0.977/-0.211$[d] $c_1/c_2 = 0.953/-0.168$ for CI at $T = 20$ μh	

[a] Throughout this paper all energy values are given in hartrees unless specified otherwise. The secular equation sizes to be solved in the CI are generally given in parentheses together with the $E(T)$ values.

[b] See Section 3.4.

[c] The core represents the number of orbitals which always remain doubly occupied in the CI treatment, the valence set consists of those orbitals which are allowed variable occupation in the CI.

[d] c_1, c_2 refers to the coefficients in the 2×2 CI and also to those of the corresponding configurations in the final CI treatment.

Table 1b. Variation of the total CI energy as a function of the threshold value T for the $^3\Sigma_g^-$ and $^1\Delta_g$ states in O_2 at two different internuclear distances R. (Notation as in Table 1a)

O_2 Molecule, $R = 2.28$ bohrs				O_2 Molecule, $R = 4.88$ bohrs		
$T \times 10^{-6}$	$^3\Sigma_g^-$	$^1\Delta_g$	ΔE_e (eV)[a]	$^3\Sigma_g^-$	$^1\Delta_g$	ΔE_e (eV)[a]
20	−149.80297(306)	−149.76408(244)	1.058	−149.62819(340)	−149.63161(273)	−0.093
10	−149.80456(381)	−149.76572(301)	1.057			
5	−149.80545(493)	−149.76664(382)	1.056	−149.63083(547)	−149.63425(426)	−0.093
2	−149.80599(641)	−149.76725(495)	1.054			
SCF = −149.61537 $^3\Sigma_g^-$ INO's (Ref. [5])[b], 4 Mains core = 4 valence set = 18				SCF = −149.56808 $^3\Sigma_g^-$ NO's, 6 Mains core = 4 valence set = 18		

[a] Energy difference between the $^3\Sigma_g^-$ and $^1\Delta_g$ states.

[b] Selection for the NO's on $^3\Sigma_g^-$ basis with $T = 1 \times 10^{-6}$ hartree, three iterations.

transition energies between different states at the same nuclear geometry or potential energy variations for a single state along a particular geometrical path that selection techniques appear to offer the greatest promise, simply because there is a reasonable hope that the effects of the neglected configurations tend to cancel each other in such energy *comparisons*. Yet a further look into this question for various states of ethylene (both for planar and perpendicular conformations thereof) shows that even such energy *differences* can vary significantly with the

Table 2. Calculated properties for the CN molecule as a function of the threshold value T (in hartrees) in the CI calculation

Properties[a]	$T = 50 \times 10^{-6}$	$T = 20 \times 10^{-6}$	$T = 10 \times 10^{-6}$
$E(T)$ for $^2\Sigma^+$	−92.2956	−92.2966	−92.2969
Sec. eq. size	(133)	(160)	(175)
$\langle x \rangle$	0.7491	0.7506	0.7505
$\langle xx \rangle$	7.9834	7.9869	7.9877
$\langle yy \rangle = \langle zz \rangle$	8.1890	8.1927	8.1915
kinetic energy	91.8098	91.8080	91.8139
$\lvert\langle \psi(^2\Pi) \lvert \Sigma r_i \rvert \psi(^2\Sigma) \rangle\rvert^2$	0.245	0.247	0.248
$\lvert\langle \psi(^2\Pi) \lvert \Sigma V_i \rvert \psi(^2\Sigma) \rangle\rvert^2$	0.0279	0.0260	0.0298

[a] Calculation of properties carried out with $^2\Sigma^+$ SCF MO's, those of transition moments with $^2\Pi$ MO's; 1 main configuration, core = 3, valence set = 13, 23 AO's.

Table 3. Energy differences ΔE (in eV) between several states of ethylene as a function of the energy cut-off value T (in hartree)

$T \times 10^{-6}$	100	80	60	40	20
C_2H_4, $\theta = 90°$ $R = 1.5$ Å[a]					
$^1B_1$ hartree	−78.04430	−78.04913	−78.05385	−78.06118	−78.06806
	(531)	(606)	(709)	(937)	(1312)
$\Delta E(^1B_1, {^1A_1})$	3.462	3.466	3.428	3.429	3.448
C_2H_4, $\theta = 0°$ $R = 1.35$ Å					
$\Delta E(^1A_g, R)$[b]	7.537	7.397	7.275	7.233	7.187
	(846)	(1024)	(1256)	(1498)	(1918)
$\Delta E(^1A_g, V_u)$	8.434	8.437	8.420	8.364	8.336
	(666)	(744)	(863)	(1139)	(1704)
$\Delta E(^1A_g, V_g)$	8.129	8.029	7.929	7.857	7.814
	(396)	(470)	(587)	(722)	(933)
$\Delta E(^1A_g, R')$	9.086	8.935	8.819	8.784	8.735
	(846)	(1024)	(1256)	(1498)	(1918)
$\Delta E(^1A_g, V'_u)$	10.355	10.256	10.274	10.207	10.040
	(666)	(744)	(863)	(1139)	(1704)

[a] CI calculation is based on NO's obtained from a $^1B_2$ calculation with $T = 200$ μh; see also Table 14.

[b] The total energies and sizes of secular equations for the ground state are given in Table 1a; the secular equation sizes given in parentheses refer to the CI calculation for the upper states in each case. [$R \equiv (\pi \rightarrow 3s)$, $V_u \equiv (\pi \rightarrow \pi^*)$, $V_g \equiv (\pi \rightarrow 3py)$, $R' \equiv (\pi \rightarrow 3d\sigma)$, $V'_u \equiv (\pi \rightarrow 2\pi^*)$]. In all cases core = 2, valence set = 26, 32 AO's.

value of T (Table 3); for the R', V'_u and V_g upper states the transition energy is calculated to decrease by over 0.3 eV as T is lowered from 100–20 μh. Clearly not all states show the same energy behavior with systematic lowering of the energy cut-off value[2].

Furthermore, binding energy results appear to be even more sensitively tied to the value of T, as is illustrated in Table 4, in which both equilibrium and

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[2] To what extent the choice of MO's plays a role will be discussed later in Section 3.4.

Table 4. Energy differences between different nuclear conformations of the ($C_2H_4 + NH_2$) system as a function of the energy cut-off value T (in hartree)

$T \times 10^{-6}$	Energy relative to fragments for	
	Transition state	Equilibrium C_2NH_6
100	32.9 (kcal)	29.4 (kcal)
50	25.5	15.9
40	24.2	12.1
30	23.4	8.9
20	21.9	4.9
10	18.9	0.0
(0)	16.0	− 3.1

1 Main, core = 3, valence set = 18, 24 AO's.

transition state conformers of the C_2NH_6 system are compared with their respective separated fragments ethylene and NH_2. Clearly the total energy converges much faster for the separated species as a unit than for either of the other conformers of interest. The example cited earlier in Table 1b for O_2 provides a counterexample to this behavior but again it must be concluded that *in general* even the energy difference results of such selected CI calculations are not satisfactorily independent of T, particularly when greatly different nuclear arrangements are being compared; the uncertainty appears to be less critical for vertical transition energy results, however.

3.2. Extrapolation to Zero Threshold

Whenever the final truncated-CI energy differences between comparative systems are found to vary strongly with the energy cut-off value T, there naturally arises a serious question as to just which set of CI results is most reliable. An obvious way out of this dilemma would be the effective elimination of the threshold T as a parameter in the CI treatment; one means of accomplishing this objective is to take advantage of the information available from the ΔE_r values for all neglected configurations, as defined in Eq. (6).

For example, if the sum of these quantities is simply added to the corresponding calculated CI energy result in each case for the aforementioned C_2NH_6 structures, the ensuing extrapolations to zero threshold are seen to lead to quite consistent estimates of the relative stabilities of the separated fragments, transition state, and combined β-aminoethyl radical (Table 5); clearly the extrapolated energy differences for each value of T give a much better idea of the magnitude of the desired quantities than do the corresponding truncated CI results of Table 4, which vary by as much as 32 kcal/mole for the extremum T values in this case.

If the same type of extrapolation procedure is used for the calculations described in Table 3 it is easily seen that the consistency of the absolute results for $E(T \to 0)$ is not as good (Table 6) as in the foregoing C_2NH_6 case, although the discrepancies in all cases do not exceed 0.008 hartree for comparison of corresponding results obtained at the highest and lowest values of T undertaken. Even more significantly perhaps, the changes in $E(T \to 0)$ are monotonic in

Table 5. Energy values $E(T)$ as a function of the threshold value T and corresponding extrapolated data $E(T \rightarrow 0)$ for different C_2NH_6 nuclear conformations

	$T \times 10^{-6}$	$E(T)$	N^a	$E(T \rightarrow 0)$
$C_2NH_6^{\bullet}$ Equilibrium	100	−133.5720	341	−133.6256
	50	−133.5941	650	−133.6254
	40	−133.6004	788	−133.6255
	30	−133.6061	936	−133.6258
	20	−133.6131	1219	−133.6258
	10	−133.6203	1710	−133.6259
	0		3831	
$C_2NH_6^{\bullet}$ Transition state	100	−133.5665	376	−133.5973
	50	−133.5787	573	−133.5947
	40	−133.5811	630	−133.5946
	30	−133.5829	688	−133.5945
	20	−133.5859	803	−133.5945
	10	−133.5907	1096	−133.5954
	0		3831	
$NH_2^{\bullet} + C_2H_4$ Fragments	100	−133.6189	209	−133.6210
	50	−133.6194	220	−133.6206
	40	−133.6197	228	−133.6206
	30	−133.6203	244	−133.6206
	20	−133.6208	250	−133.6209
	10	−133.6208	250	−133.6209
	0		3831	

[a] Size of secular equation. All energy values in hartree.

T itself, becoming ever somewhat greater as this quantity is further decreased. As a result the *extrapolated* energy *differences* between various states remain nearly constant regardless of the cut-off energy actually employed as the selection criterion. Analogous extrapolated results for various O_2 states given in Table 7 show very much the same behavior as in the case of the ethylene calculations, with the exception that the discrepancies between corresponding $E(T \rightarrow 0)$ values are larger than those observed before; again a monotonic and fairly regular increase in the extrapolated energy is observed as the cut-off value is decreased.

Taken together these results indicate that the $E(T \rightarrow 0)$ values are still in general too dependent on the actual value of T chosen to justify the use of a *single* truncated CI calculation, *even after extrapolation* on the basis of the ΔE_r values for the neglected configurations is carried through. Yet it is quite clear from Figs. 1a, b, in which these extrapolated energy values $E(T \rightarrow 0)$ are plotted as a function of the actual T value for various ethylene states, that there is good reason to believe that a series of such $E(T \rightarrow 0)$ values can be used to obtain a quite accurate value for $E(0)$ itself[3].

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[3] That is, the energy in a CI in which all single- and double-excitation species with respect to each of the main configurations employed in the treatment are included.

Table 6. Energy contribution $\Sigma\,\Delta E_r$ of the neglected configurations and extrapolated $E(T\rightarrow 0)$ values as a function of the threshold value T for a number of states in ethylene

$T \times 10^{-6}$		100	80	60	40	20	Sec. Eq. Size $T\rightarrow 0$
C_2H_4, $R = 1.5$ Å $\theta = 90°$							
$^1B_1$	$\Sigma\,\Delta E_r$	0.0421	0.0367	0.0314	0.0227	0.0142	
	$E(T\rightarrow 0)$	−78.0864	−78.0858	−78.0853	−78.0839	−78.0823	9697 (4M)[a]
$^1A_1$	$\Sigma\,\Delta E_r$	0.0418	0.0356	0.0285	0.0182	0.0098	
	$E(T\rightarrow 0)$	−77.9589	−77.9573	−77.9563	−77.9534	−77.9511	9697 (4M)
C_2H_4, $R = 1.35$ Å $\theta = 0°$							
^1A_g	$\Sigma\,\Delta E_r$	0.0189	0.0164	0.0126	0.0083	0.0041	
	$E(T\rightarrow 0)$	−78.1882	−78.1873	−78.1871	−78.1867	−78.1860	2105 (2M)
R[b]	$\Sigma\,\Delta E_r$	0.0342	0.0263	0.0182	0.0119	0.0058	
	$E(T\rightarrow 0)$	−77.9265	−77.9255	−77.9254	−77.9244	−77.9236	4043 (2M)
V_g	$\Sigma\,\Delta E_r$	0.0338	0.0271	0.0190	0.0121	0.0061	
	$E(T\rightarrow 0)$	−77.9043	−77.9030	−77.9022	−77.9018	−77.9009	2282 (1M)
V_u	$\Sigma\,\Delta E_r$	0.0266	0.0241	0.0189	0.0118	0.0056	
	$E(T\rightarrow 0)$	−77.8859	−78.8850	−77.8840	−77.8828	−77.8811	6043 (3M)
R'	$\Sigma\,\Delta E_r$	0.0334	0.0253	0.0176	0.0117	0.0057	
	$E(T\rightarrow 0)$	−77.8688	−77.8679	−77.8680	−77.8673	−77.8666	4043 (2M)
V_u'	$\Sigma\,\Delta E_r$	0.0391	0.0339	0.0299	0.0222	0.0112	
	$E(T\rightarrow 0)$	−77.8278	−77.8280	−77.8269	−77.8254	−77.8241	6043 (3M)

[a] A set of 4 main configurations was used (core = 2, valence set = 26, in each case).

[b] For notation see also Table 3.

In principle, of course, a plot of $E(T)$ itself versus T should give a fairly good estimate of the zero-threshold energy, but it is obvious from the foregoing tables and figures (including Fig. 2) that the variations in this quantity are much larger than for analogous $E(T\rightarrow 0)$ data, so that an extrapolation on the basis of the raw $E(T)$ results is expected to be significantly less effective[4].

In either case it is clearly necessary to solve secular equations corresponding to a *series* of T values and not just a single equation for a specific T as originally envisioned. On the other hand, this objective can be achieved with very little additional computational effort once the solution of the largest secular equation, that is the one corresponding to the smallest value of T, is explicitly solved; no additional matrix elements are required, of course, and by judicious use of the eigenvector(s) obtained from the equation corresponding to the

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[4] The fact that $E(T\rightarrow 0)$ appears to be quite generally a monotonically increasing function of T while $E(T)$ itself is necessarily monotonically decreasing as T is lowered clearly leads to a situation in which the two types of extrapolation procedures neatly complement one another, approaching the desired zero-threshold energy value from opposite directions.

In fact, this procedure can be generalized by defining a quantity $E_\lambda(T\rightarrow 0) = E(T) + \lambda \sum_r \Delta E_r$ with constant λ, where $\lambda = 0$ corresponds to the uncorrected $E(T)$ values and $\lambda = 1$ to those corrected according to Eq. (8). The entire family of $E_\lambda(T\rightarrow 0)$ curves approaches the desired limit $E(0)$ at the zero threshold. This arbitrariness in the choice of λ can then be used to construct the most *slowly varying* $E_\lambda(T\rightarrow 0)$ curve possible, thereby allowing for the most *convenient extrapolation* to $E(0)$.

Table 7. CI energy $E(T)$ at different energy cut-off values T and corresponding extrapolated value $E(T \to 0)$ for O_2 in its three lowest electronic states

	$T \times 10^{-6}$	$E(T)$	N^a	$E(T \to 0)$
$O_2, {}^3\Sigma_g^-$	100	−149.8491	667	−149.9078
(1 Main)	80	−149.8547	768	−149.9045
	60	−149.8575	844	−149.9018
	40	−149.8678	1173	−149.8964
	20	−149.8750	1617	−149.8907
			5032	(−149.8840 − 149.8845)
$O_2, {}^1\Delta_g$	100	−149.8129	562	−149.8540
(2 Mains)	80	−149.8170	645	−149.8509
	60	−149.8231	782	−149.8475
	40	−149.8266	917	−149.8445
	20	−149.8326	1261	−149.8410
	0		2893	(−149.8365 − 149.8370)
$O_2, {}^1\Sigma_g^+$	100	−149.7901	562	−149.8314
(2 Mains)	80	−149.7940	645	−149.8281
	60	−149.8000	782	−149.8247
	40	−149.8037	917	−149.8219
	20	−149.8093	1261	−149.8180
	0		2893	(−149.8140 − 149.8145)

[a] Size of secular equation. In all cases core = 2, valence set = 30, 34 AO's; the ${}^3\Sigma_g^-$ NO's form the basis of the CI calculation, which was carried out in D_{2h} symmetry in this case.

Table 8. Extrapolated energies $E(T \to 0)$ and energy contribution $\Sigma\, \Delta E_r$ of neglected configurations at different threshold values T for two states of the perpendicular C_2H_4 conformer; also listed for comparison are expansion coefficients[a] of the two dominant configurations in both ψ_0 and $\psi(T)$

$T \times 10^{-6}$	60	50	40	20	0
$C_2H_4, R =$ 1.5 Å					
$\theta = 90°$					
${}^1B_2$, NO's[b]					
$\Sigma\, \Delta E_r$	0.0173	0.0140	0.0111	0.0064	0.0000
$E(T \to 0)$	−77.9500	−77.9492	−77.9499	−77.9476	(−77.946)
Sec. Eq. Size	860	959	1063	1325	10915
${}^1A_1$, NO's[b]					
$\Sigma\, \Delta E_r$	0.0168	0.0136	0.0109	0.0063	0.0000
$E(T \to 0)$	−77.9530	−77.9522	−77.9510	−77.9501	(−77.949)

${}^1B_2$, 2×2 CI: $c_1/c_2 = 0.418/-0.896$
final CI: $c_1/c_2 = 0.929/-0.199$

${}^1A_1$, 2×2 CI: $c_1/c_2 = 0.896/\ 0.424$
final CI: $c_1/c_2 = 0.201/\ 0.930$

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[a] Calculations carried out in C_{2v} symmetry so that ${}^1A_1$ and ${}^1B_2$ states are obtained from the same secular equation.

[b] Approximate NO's are obtained from a calculation on the ${}^1B_2$ state at $T = 100$ μh with subsequent diagonalization of the density matrix. Four main configurations are used in the final CI. A non-symmetric basis has been chosen in this instance.

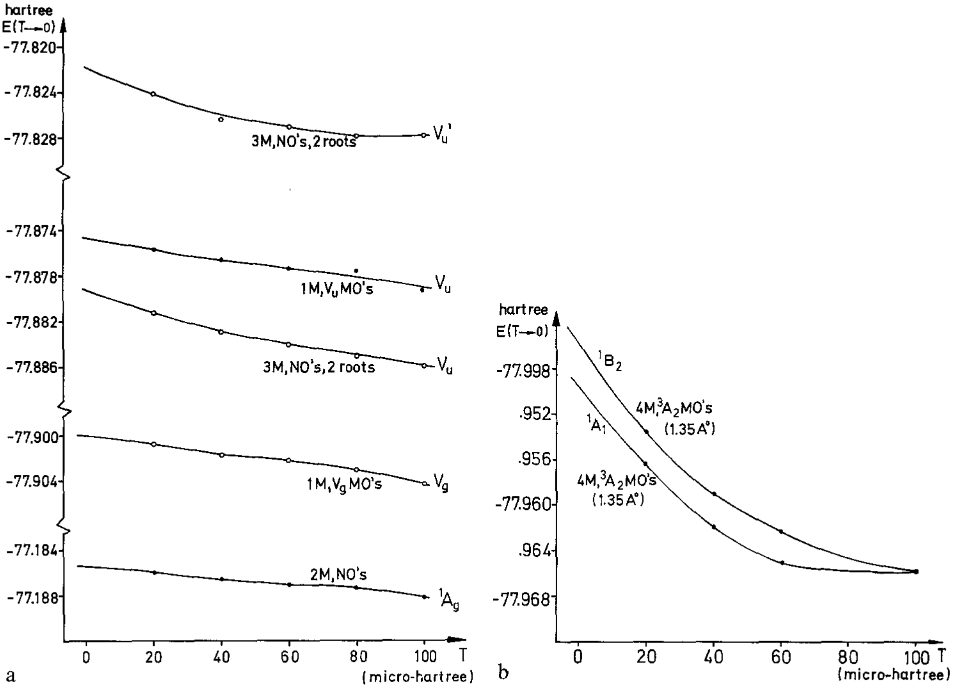

Fig. 1a and b. Extrapolated energies $E(T \to 0)$ as a function of the energy cut-off value T employed in the selection process obtained from several CI calculations for various states of ethylene in its planar a and its perpendicular nuclear conformation b. [^1A_g is the D_{2h} ground state, V_g refers to the $^1(\pi, 3py)$ state, V_u and V_u' to the $^1(\pi, \pi^*)$ and $^1(\pi, 2\pi^*)$ states respectively; $^1A_1$ and $^1B_2$ states result from an e^2 configuration. The number of main configurations and the types of basis functions used in the CI calculations is indicated at each curve]

smallest T value those species deriving from the higher-threshold equations can be obtained in a very small number of iterations in the Nesbet-Shavitt procedure [8]. In this way it is possible to effectively remove the influence of the energy cut-off value T on the final CI energy results, an objective which has been shown to be highly desirable (if not indeed necessary) in view of the calculated findings discussed above.

As mentioned in Section 2.1 there are of course other areas of uncertainty in such selection methods which also must be investigated, particularly the importance of the choice of main configurations and the influence of the MO basis set used in the calculation as a whole. While these points will be taken up in the remaining part of this section, comment on one such aspect is pertinent at this point, namely to what extent the magnitude of the ΔE_r values is affected by the degree to which the final wavefunction $\psi(T)$ in Eq. (7) can be approximated by ψ_0 itself, a question which is obviously critical in making the transition to Eq. (8) in Section 2.3. The results of Table 8 for the $^1A_1$ and $^1B_2$ states of C_2H_4 at $\theta = 90°$ indicate that at least as long as the most important configurations are included in expansions of both ψ_0 and $\psi(T)$ there is no particular requirement

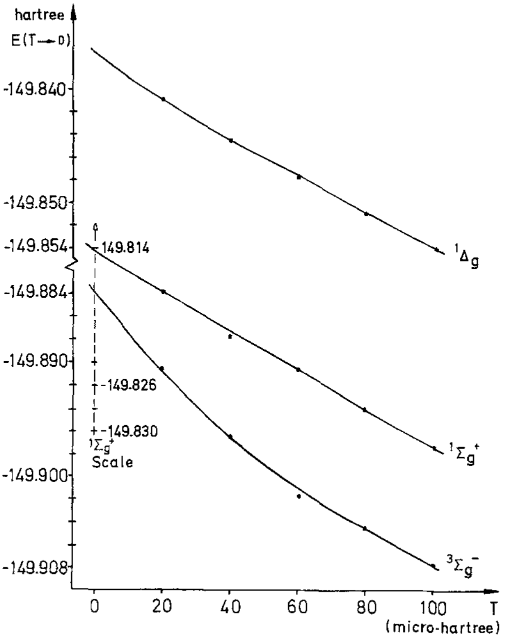

Fig. 2. Extrapolated energies $E(T\to 0)$ as a function of the energy cut-off value T employed in the selection process obtained from CI calculations for three states of O_2. ($R=2.28$ bohr, 1 main configuration, $^3\Sigma_g^-$ NO's)

that the overlap between these two approximate wavefunctions be especially great to allow for sufficiently accurate estimation of the energy contributions of the neglected configurations. The mixing coefficients in this instance are greatly different in the small 2×2 zero-order secular equation (i.e. in ψ_0) than their corresponding values in the final CI for $\psi(T)$, and yet the behavior of the $E(T\to 0)$ results is not very noticeably different than in other cases discussed previously for which only a small change in the relative weighting of the main configurations is observed in the analogous comparison.

Finally, the actual values of T to be used in implementing the aforementioned extrapolation technique deserve some consideration. A simple plot of the number of configurations included in a given secular equation as a function of T for various cases (Fig. 3) shows quite clearly that there is generally a rapid increase in the number of configurations selected as T reaches the 20–40 μh range. In order to be effective the selection technique must employ a cut-off value which eliminates as high a number of test species as possible consistent with the necessity of allowing for a reliable extrapolation to zero threshold. Results such as those in Fig. 3 when compared to the data of Figs. 1 and 2 for energy extrapolations suggest strongly that one can safely employ minimum T values of 20 μh (or perhaps somewhat larger) without jeopardizing the accuracy of the CI energy extrapolations and while still holding the secular equation orders to easily manageable values (from 1000–2000, for example, for systems considered in this work). Generally speaking as the size of the basis set increases it becomes

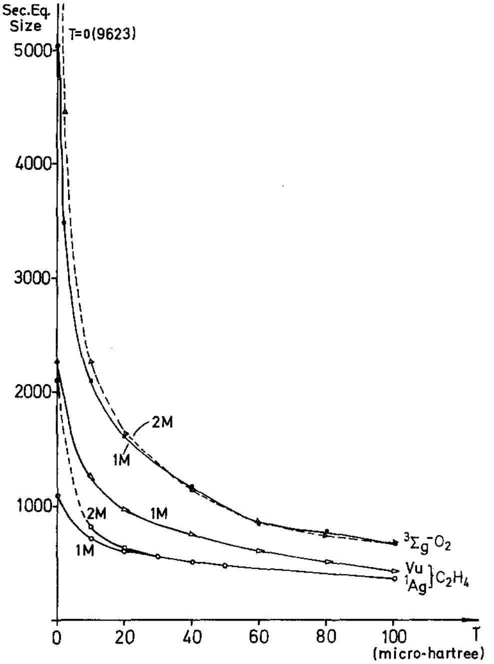

Fig. 3. Secular equation size for several CI calculations for different states of molecules as a function of the energy cut-off value T employed in the selection process

more critical to resort to relatively small T values, since the number of neglected configurations (at a given threshold) is thereby substantially increased. Comparison of results for ethylene using double-zeta basis sets with and without additional polarization (s, $p\pi$ and $d\pi$) functions, for example, indicate that the $E(T\rightarrow 0)$ results vary nearly twice as fast with T in the larger basis (for a variety of states). Nevertheless, even at that, no appreciable difference in the smootheness of the corresponding $E(T\rightarrow 0)$ curves is observed between these two cases and hence it would appear that the overall effectiveness of the present extrapolation method is not significantly dependent on the nature of the AO basis used in the calculations[5].

3.3. Importance of Choice of Main Configurations

Assuming that reliable prediction of the zero-threshold energy $E(T)$ is possible by the methods discussed above, there still remains the important question of how large the set of main configurations need be in a given case. Because of the selection technique employed it is obvious that no test configuration which corresponds to *at least* a triple excitation with respect to *all* the main species can

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[5] Throughout this paper basis sets of double-zeta quality have generally been used, with the exception of the C_2NH_6 calculations, in which a single-zeta (fixed group gaussian) species is employed, and also those for O_2, in which polarization functions are included in the otherwise double-zeta set.

possibly result in a non-zero ΔE_r value, and hence it is useless to even generate such higher excitation configurations. In other words, in order to account for those configurations which can *only* interact in an *indirect* manner with the *leading* configuration in a given state (because they result from quadruple excitations relative to this species, for example) it is necessary to add more main configurations to the $\{\phi_m\}$ subset which actually do interact *directly* with such a test species. The addition of more mains to the original set is thereby seen as a quite efficient manner of introducing important higher excitation species (relative to the leading configuration) into the final CI.

The effect of increasing the set of main configurations has first been investigated in the calculations for the C_2NH_6 structures discussed earlier (Tables 4 and 5); in each case the configuration with the second largest coefficient in the final CI expansion has been added as a second main species. It is obvious from Table 9 that the secular equation sizes do not change markedly in any of the three cases upon expanding the $\{\phi_m\}$ subset used for the selection process. Furthermore, and certainly not at all surprisingly, the effect on $E(T)$ is seen to increase substantially with the magnitude of the mixing coefficient of the added main configuration. Finally and most importantly, it is seen from the C_2NH_6 and also the C_2H_4 ^1A_g results that the full effect of the added main species is not really apparent until extrapolation to zero threshold is carried through; again this result is to be expected since the ΔE_r values for those species which do not interact directly with the leading term are presumably relatively small even after suitably interacting species of lesser importance are added to the set of main configurations.

From the second of the above remarks it is clear that the reliability of the overall CI treatment is improved significantly when the set of main configurations consists of all those species which have a relatively large expansion coefficient (say greater than 0.1) in the final CI. Proceeding in such a way thus easily allows one to expand the scope of the final CI to much larger limits (via extrapolation techniques) without greatly increasing the size of the secular equations which eventually have to be solved. The amount of computation needed for the selection process is of course increased if a large set of main configurations is employed, but this phase of the calculation represents only a small portion of the total computational effort and thus there is really little to deter one from expanding the treatment in this manner, especially when a relatively large number of configurations are characterized by a fairly significant mixing coefficient in the CI wavefunction. Corresponding investigations for C_2H_4 and O_2 (also considered in Table 9) certainly tend to substantiate these quite general conclusions in every case.

If more than one root of a given symmetry type is desired it is obviously important to include in the set of main configurations all those species which play a leading role in the representation of *any* of the desired states. Furthermore, it is found that even such measures are not sufficient in themselves to ensure a proper treatment of all the desired roots; in addition it is necessary that the actual selection technique be based on the energy lowerings of *each* root, as described in Section 2.1. The effect of multiple-root selection for various $^1A_1$ states of thioformaldehyde [9] and formaldehyde as well as for several

Table 9. Comparison of energy values obtained by employing a different number of main configurations, and corresponding mixing coefficients in ψ_0 and $\psi(T)$

				Ratio between leading coefficients
	E (1 Main)	E (2 Main)	ΔE	
C_2NH_6 Equilibrium				
$E(T=50)$	-133.5941 (650)	-133.5937 (643)	0.0004	$c_1/c_2 = 0.9980/0.0625$
$E(T \rightarrow 0)$	-133.6254 (3831)	-133.6255 (7387)	-0.0001	$c_1/c_2 = 0.9707/0.0554$
Transition state				
$E(T=50)$	-133.5787 (573)	-133.5801 (562)	-0.0014	$c_1/c_2 = 0.9932/0.1165$
$E(T \rightarrow 0)$	-133.5947 (3831)	-133.5982 (7387)	-0.0035	$c_1/c_2 = 0.9361/0.1012$
$NH_2 + C_2H_4$				
$E(T=50)$	-133.6194 (220)	-133.6220 (248)	-0.0026	$c_1/c_2 = 0.9698/0.2438$
$E(T \rightarrow 0)$	-133.6206 (3831)	-133.6260 (7387)	-0.0054	$c_1/c_2 = 0.9509/0.1894$
	E (4 Mains)	E (6 Mains)	ΔE	
O_2 Molecule, ${}^3\Sigma_g^-$				
$E(T=20)$				
$R = 2.48$, ${}^3\Sigma_g^-$ NO's	-149.7969 (334)	-149.7969 (331)	0.0000	$c_5, c_6 < 0.1$
$R = 2.88$, ${}^5\Sigma_g^+$ SCF MO's	-149.7199 (322)	-149.7203 (338)	-0.0004	$c_5 = 0.12$, $c_6 < 0.08$
$R = 3.28$, ${}^5\Sigma_g^+$ SCF MO's (distances in bohr)	-149.6742 (401)	-149.6766 (407)	-0.0024	$c_5 = 0.19$, $c_6 = 0.15$
	E (1 Main)	E (2 Mains)	ΔE	
C_2H_4, ${}^1A_g$ ground state				
$E(T=20)$	$-$ 78.1764 (612)	$-$ 78.1776 (632)	-0.0012	$c_1/c_2 = 0.9874/0.1581$
$E(T \rightarrow 0)$	$-$ 78.1789 (1099)	$-$ 78.1826 (2105)	-0.0037	$c_1/c_2 = 0.9574/0.1202$
	E (2 Mains)	E (4 Mains)	ΔE	
C_2H_4, $\theta = 90°$ ${}^1A_1$ $E(T=50)$ $R = 1.50$ Å	$-$ 77.9315 (954)	$-$ 77.9314 (956)	-0.0001	
	2 Main CI: $c_1/c_2 = 1/\sqrt{2}\,/\,1/\sqrt{2}$ $c_1/c_2/c_3/c_4 = 0.674/0.674/0.065/0.065$			
	4 Main CI: $c_1/c_2/c_3/c_4 = 0.706/0.706/0.029/0.029$ $c_1/c_2/c_3/c_4 = 0.675/0.675/0.065/0.065$			

Table 10. Comparison of transition energies for single-root and multiple-root selection process in different molecules

Molecule/State	SCF MO's employed	ΔE (eV) Selection is based on	
		lowest $^1A_1$ root	3 lowest $^1A_1$ roots
H_2CS, 1 $^1A_1$ (ground state)[a]	G. state	0.053 (127)	0.000[d] (286)
zero = −436.5317 hartree	$^3(\pi, \pi^*)$	0.036 (133)	0.006 (274)
	$^3(n, px_R)$	0.273 (160)	0.258 (265)
2 $^1A_1$ (n, px_R)	G. state	8.58 (127)	7.03 (286)
	$^3(\pi, \pi^*)$	8.23 (133)	6.93 (274)
	$^3(n, px_R)$	7.02 (160)	6.37 (265)
3 $^1A_1$ (π, π^*)	G. state	9.86 (127)	7.92 (286)
	$^3(\pi, \pi^*)$	8.85 (133)	8.02 (274)
	$^3(n, px_R)$	8.04 (160)	7.93 (265)
C_2H_4, Equ. geometry[b]			
1 $^1(\pi, \pi^*)$ (V_u state)	V_u state	0.097 (975)	0.000[d] (1922)
2 $^1(\pi, \pi^*)$ (V_u' state)	V_u state	4.745 (975)	1.607 (1922)
zero = −77.8746 hartree			
H_2CO, 1 $^1A_1$ (ground state)[c]	G. state	0.079 (292)	0.000[d] (1157)
zero = −113.94252			
2 $^1A_1$ (n, px_R)	G. state	12.83 (292)	8.09 (1157)
3 $^1A_1$ (π, π^*)	G. state	13.11 (292)	11.07 (1157)

[a] Details about notation and make-up of CI can be found in Ref. [9] (core = 8, valence set = 14).
[b] Core = 2, valence set = 26, 3 Mains, 32 AO's.
[c] Core = 4, valence set = 19, 5 Mains, $T = 20$, 30 AO's.
[d] Zero-energy reference point for all calculations in the table for this molecule.

$^1(\pi, \pi^*)$ species in ethylene can be judged from Table 10. In the case of H_2CS the transition energy results for $^1(n, px_R)$ and $^1(\pi, \pi^*)$ species are seen to be lowered by more than 1.0 eV (for most choices of MO basis sets) as a result of the multiple-root selection. Quite similar results are noted for H_2CO while in the case of the $^1(\pi, \pi^*)$ states of C_2H_4 the species denoted by V_u' has its energy lowered by over 3.0 eV once selection is made on the basis of the second root in the test secular equations as well as on the first. In addition the H_2CS and H_2CO results indicate that the transition energy data for the 2 $^1A_1$ and 3 $^1A_1$ species are considerably less sensitive to the choice of the MO basis when configuration selection is based on a multiple-root criterion.

If the SCF MO's of the leading configuration are used as the MO basis for the CI there is an additional consideration to be taken into account in the choice of the main configurations, arising from the fact that Brillouin's theorem prevents any direct interaction of singly excited species with the SCF configuration. It is obvious in such a case that if only this SCF species is used as ψ_0 in the selection process, no single-excitation configuration would be included in the final CI (at least for non-zero T). Because such single-excitation species can have an important influence on the properties calculated with CI wavefunctions [10] their omission is not at all desirable.

Table 11. Influence of single-excitation species on the total CI energy and their appearance in the final CI wavefunction $\psi(T)$ when different selection processes are undertaken

C_2H_4, V_u state	E (hartree)	$c_1/c_2/c_3$
1 Main, no single exc. V_u SCF MO's	−77.87185 (975)	
1 Main, with single exc. V_u SCF MO's	−77.87185 (1005)	0.963/0.085/0.037
3 Mains, 2-root selection V_u SCF MO's	−77.87496 (1922)	0.930/0.248/0.058
3 Mains, 2-root selection V_u NO's[a]	−77.87554 (1704)	0.965/0.011/0.008 3×3 CI: 0.964/−0.228/0.138

[a] NO's obtained from a CI calculation using V_u MO's, 3 Mains, 2 Roots, single exc., $T = 100$ μh.

Furthermore, there is evidence that merely providing for the inclusion of *all* such singly excited species does not completely overcome this basic difficulty connected with Brillouin's theorem. In Table 11, for example, it is seen that while several such single-excitation species are found to be characterized by relatively large coefficients in the expansion of the $^1(\pi, \pi^*)$ state of ethylene no change in the total energy of this species is observed relative to a treatment in which all the single-excitation configurations (relative to the SCF wavefunction for this state) are simply ignored. Yet when *multiple-root* selection is carried out to obtain the lowest two roots of this symmetry it is found that a significantly lower energy for the original state (first root) ensues, as well as a much larger weighting factor for the two most important single-excitation species in the corresponding CI wavefunction. This result shows that the true weight of the single-excitation species cannot be ascertained unless some means is provided for allowing configurations which do interact strongly with them to be selected for the final CI. Selecting on the basis of the lowest two roots clearly enhances this possibility for the $(\pi, 2\pi^*)$ configuration, since this species not only makes an important contribution to the lowest energy (π, π^*) state but also serves as the *leading* term in the second most stable species of this type. In other cases a similar effect can be obtained if one or more additional main configurations (invariably doubly excited species) can be found which are capable of interacting directly with both the leading term and its associated single-excitation species.

Alternatively one can use a set of orbitals other than the aforementioned SCF species, particularly some approximate natural orbitals, for which Brillouin's theorem is not valid (Table 11). This procedure is generally preferable, since after all the mere fact that such single-excitation species are so important in a CI based on the SCF MO's obviously implies that the NO's are significantly more effective for the expansion of the multi-configuration wavefunction of the state in question. In this connection it is interesting that in Table 11 the final CI weighting of the single-excitation $(\pi, n\pi^*)$ species is considerably reduced by transferring from the SCF MO basis to that of the NO's. Thus in the last analysis the question raised by the effects of Brillouin's theorem is really not so much concerned with the choice of main configurations in the selection procedure as it is with the choice of MO basis in the CI itself[6]. This observation thus leads naturally to consideration of how this choice of orbitals influences the selection procedure in the general case.

3.4. *Choice of the* MO *Basis*

To the extent that the configuration selection procedure approaches the results of a full valence CI, the choice of the MO basis in the overall treatment obviously becomes less and less critical. Comparison of the CI results for the ground state of ethylene obtained by using respectively the SCF MO's of the ground state itself and those of the V_u $^1(\pi, \pi^*)$ species demonstrates this point quite well (Table 12), with the total energy values in the two cases progressively coming into better agreement as the number of main configurations is increased. The fact remains, however, that there is a distinct advantage in using the most suitable MO basis for the calculations, if only to keep the size of the final CI at a given value of T at the smallest possible level (see Table 12).

With this objective in mind it is interesting to investigate the effect of using approximate natural orbitals in the CI. Such species can be obtained, for example, in an iterative scheme (INO) first introduced by Bender and Davidson [11] by diagonalizing the first-order density matrix for the desired state (using a fixed set of configurations chosen from experience) [12]. The selection technique can also be used in this connection to automate the choice of the configuration set employed, as has recently been demonstrated [5] in work on O_2; in particular to allow for a specific selection at a given geometry, a precaution which certainly seems warranted in view of the general alteration in the wavefunction representation which is observed as geometrical changes occur. In general at least four or

Table 12. Comparison of ground state energies for C_2H_4 obtained from equivalent CI calculations based on different sets of MO's

	G.S. MO's	V_u MO's	ΔE
Single configuration	-78.0009 (1)	-77.9559 (1)	0.045
3×3 CI	-78.0156^{a} (3)	-77.9783 (3)	0.037
1 Main, $T = 20 \times 10^{-6}$	-78.1764 (612)	-78.1671 (647)	0.009
$T \to 0$	-78.1789 (1099)	-78.1693 (1099)	0.009
3 Mains, single exc. incl.			
$T = 20 \times 10^{-6}$	-78.1775 (632)	-78.1680 (729)	0.009
$T \to 0$	-78.1826 (4057)	-78.1763 (4057)	0.006

[a] The third main configuration is not important in this case; a 2×2 CI yields the same energy.

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[6] The use of NO's to obtain *both* the first and higher roots for a given symmetry type is itself fraught with certain fundamental difficulties because of the requirement that the corresponding wavefunctions be orthogonal. If the NO's are significantly different for two (or more) roots of the same symmetry use of one or the other set will inevitably lead to a rather diffuse representation of the complementary state(s). In this situation the procedure of adding more main configurations in order to improve the selection process for each of the complementary roots can be quite effective in bringing the treatment of all these species into balance while still satisfying the orthogonality constraints and without greatly increasing the size of the necessary computations.

Table 13. Comparison of energy values for the ground state of ethylene at different threshold values employing NO's of the first and second macro-iteration

$T \times 10^{-6}$	NO (1)[a]		NO (2)[b]	
	$E(T)$	$E(T \to 0)$	$E(T)$	$E(T \to 0)$
100	−78.1693 (283)	−78.1882	−78.1695 (279)	−78.1877
80	−78.1709 (312)	−78.1873	−78.1724 (317)	−78.1872
60	−78.1746 (366)	−78.1871	−78.1745 (353)	−78.1868
40	−78.1784 (454)	−78.1867	−78.1782 (435)	−78.1866
20	−78.1819 (597)	−78.1860	−78.1818 (581)	−78.1859
0		−78.1850 −78.1852		−78.1850 −78.1852

[a] NO's obtained by diagonalization of the density matrix resulting from a CI calculation for the ground state of C_2H_4 (2 Mains) using ^1A_g SCF MO's and $T = 100 \times 10^{-6}$ hartrees.

[b] NO's obtained from the equivalent calculation using the NO (1) species.

five iterations are required before convergence is obtained in this procedure; usually only a rather small CI including all single-excitation species with respect to a series of main configurations is carried out in such calculations.

The results discussed above suggest a different approach to this problem, however, which does not rely on an iterative procedure, namely to simply carry out a single CI calculation at a relatively high threshold (say $T = 100$ μh) in the usual way[7], and then diagonalize the resulting density matrix to obtain the approximate NO's[8]. When this is done for the ^1A_g ground state of C_2H_4 (using two main configurations in the selection process) the improvement in the $T = 20$ CI results relative to the corresponding treatment using the respective SCF MO's is significant (Table 13), with the extrapolated ($T \to 0$) energy value being 0.0035 hartree lower when the NO's are used. A second macro-iteration results in no further change in the *final* CI *energy* at any of the T values considered however, in distinct contrast to what is usually observed when the INO method is applied in the conventional manner [5].

Furthermore, in cases for which there is not as important a secondary configuration as in the example of the C_2H_4 ground state ($\pi^2 \to \pi^{*2}$) there is evidence that even the first macro-iteration does not result in any improvement in the final CI results relative to what is obtained using the SCF MO's of the leading configuration, as for example is found in the results for the $^1B_2$ state of perpendicular C_2H_4 ($R = 1.5$ Å) in Table 14; in fact, the extrapolated value for the energy ($T \to 0$) is actually slightly higher when the approximate NO's (obtained from both a $T = 200$ μh and $T = 100$ μh calculation) are used. The present results and those for other states (Table 14) suggest in addition that the

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[7] As in the iterative natural orbital method itself it is of course necessary to allow all orbitals in the initial MO basis (excluding perhaps those of inner-shell type) to have variable occupation in the associated CI treatment. One of the main advantages of the selection method in general, of course, is that by systematically neglecting a large number of weakly interacting configurations it becomes quite feasible to include all MO's resulting from a given AO basis in the valence set of the CI calculations, even at the final stage for which relatively small cut-off values are employed in the selection process.

[8] Alternative non-iterative schemes for obtaining NO's have been given by Lie *et al.* [13] and Hay [14].

Table 14. Total CI energies for several states of perpendicular C_2H_4 ($R = 1.5$ Å, $\theta = 90°$) obtained by employing approximate NO's resulting from two different high-threshold calculations of the $^1B_2$ state

MO description	$E(^1B_1)$		$E(^1A_1)$		$E(^1B_2)$	
	$E(T=20)$	$E(T\to 0)$	$E(T=20)$	$E(T\to 0)$	$E(T=20)$	$E(T\to 0)$
NO's of $^1B_2$ CI at $T=100$	-78.0699 (1296)	-78.0827 (9697)	-77.9425 (1296)	-77.9514 (9697)	-77.9380 (1201)	-77.9473 (3993)
NO's of $^1B_2$ CI at $T=200$	-78.0681 (1312)	-78.0823 (9697)	-77.9413 (1312)	-77.9511 (9697)	-77.9369 (1203)	-77.9473 (3993)
$^1B_2$ SCF MO's[a]					-77.9376 (1424)	-77.9479 (3993)

[a] The $^1B_2$ SCF MO's are used for this $^1B_2$ CI and the resulting density matrix is diagonalized to obtain the corresponding NO's.

choice of the energy cut-off value in the CI designed to *determine* the approximate NO's is not at all critical (at least judging from the extrapolated energy results in each case); hence T should be kept relatively high for this purpose to ensure that only relatively small secular equations have to be solved to achieve the desired result.

As a final example various calculations for the $^1B_1$ state of C_2H_4 ($\theta = 90°$) have been carried out (Table 15) employing different types of SCF MO's and associated NO's. As usual the SCF MO's of this state (and those of the closely related $^3A_2$ state) are found to be more efficient in the CI treatment than those of a species of substantially different character, namely of the $^1B_2$ state (second column in Table 15). The use of approximate NO's obtained for other than the $^1B_1$ state (for example for the $^1B_2$ and $^1A_1$ species) is also not as effective. One macro-iteration on the $^1B_2$ SCF MO's (i.e. a CI calculation for the $^1B_1$ state with $T = 100$ μh employing $^1B_2$ SCF MO's followed by diagonalization of the resultant density matrix) produces orbitals which lead to substantially the same final extrapolated CI energy (Column 4 of Table 15) as for the corresponding $^3A_2$ SCF MO's. Furthermore, additional macro-iterations on either the $^3A_2$ SCF MO's or the first-generation $^1B_1$ NO's as usual produce no essential change in the final CI results, as can be seen from the last and fifth columns in Table 15 respectively.

From the present results it appears that one such macro-iteration at a relatively high threshold value ($T = 100$ μh) is sufficient for all practical purposes to guarantee the best possible results *in the final* CI *calculations*. The selection procedure employed in this single iteration should be basically the same as in the corresponding final treatment, with the exception that the value of T be chosen to be significantly larger; again the choice of main configurations is most critical and the method of arriving at the proper set is no different than before (Section 3.3). In cases (such as the V_u $^1(\pi, \pi^*)$ states of planar ethylene) in which relatively low-lying single-excitation species of the same symmetry as the leading configuration exist, a multiple-root selection procedure as discussed above is helpful in order to ensure that such single-excitation secondary configurations are allowed to make their proper contribution to the wavefunction of the lowest root. This precaution is really only necessary, however, if the SCF MO's

Table 15. Calculated energy for the $^1B_1$ state of perpendicular ethylene ($R = 1.5$ Å, $\theta = 90°$) employing different MO basis sets

$T \times 10^{-6}$	2 Mains	CI basis functions, 4 Mains[c]		
		NO's from	NO's from	NO (2)'s from[b]
	$^1B_2$ SCF MO's	$^1B_2$ CI at $T = 200$ µh	$^1B_1$ CI at $T = 100$ µh[a]	$^1B_1$ CI at $T = 100$ µh
100	0.0408 (424)	0.0443 (531)	0.0526 (465)	0.0546 (476)
$T \to 0$	(0.0871)	(0.0864)	(0.0935)	(0.0931)
80	0.0475 (514)	0.0491 (606)	0.0574 (555)	0.0590 (557)
$T \to 0$	(0.0856)	(0.0858)	(0.0922)	(0.0919)
60	0.0531 (614)	0.0538 (709)	0.0613 (674)	0.0639 (715)
$T \to 0$	(0.0846)	(0.0853)	(0.0912)	(0.0901)
40	0.0609 (806)	0.0612 (937)	0.0681 (905)	0.0709 (966)
$T \to 0$	(0.0828)	(0.0839)	(0.0892)	(0.0884)
20	0.0675 (1121)	0.0681 (1312)	0.0773 (1476)	0.0779 (1515)
$T \to 0$	(0.0807)	(0.0823)	(0.0870)	(0.0871)
$E(0)$	(0.079) (5892)	(0.081) (9697)[c]	(0.085) (9697)[c]	(0.0855) (9697)[c]

$T \times 10^{-6}$		CI basis functions, 1 Main	
		NO's from[d]	NO's from[d]
	$^3A_2$ SCF MO's	$^1A_1$ CI at $T = 100$ µh	$^1B_1$ CI at $T = 100$ µh
100	0.0529 (471)	0.0480 (424)	0.0533 (394)
$T \to 0$	(0.0926)	(0.0901)	(0.0954)
80		0.0520 (487)	0.0568 (446)
$T \to 0$		(0.0884)	(0.0942)
60		0.0595 (635)	0.0638 (579)
$T \to 0$		(0.0859)	(0.0918)
50	0.0670 (954)		
$T \to 0$	(0.0899)		
40		0.0659 (826)	0.0709 (772)
$T \to 0$		(0.0827)	(0.0898)
20	0.0766 (1037)	0.0734 (1157)	0.0777 (1103)
$T \to 0$	(0.0876)	(0.0808)	(0.0874)
$E(0)$	(0.086) (4357)[e]	(0.079) (4357)[e]	(0.0855) (4357)[e]
	zero of energy: −78.000 hartree, all energy values in the table are negative		

[a] The NO's are obtained from the $^1B_1$ CI calculation employing $^1B_2$ SCF MO's and subsequent diagonalization of the density matrix.

[b] Second macro-iteration.

[c] This calculation is carried out in lower symmetry and therefore the final secular equation size is greater than in the otherwise comparable case using the $^1B_2$ SCF MO's. Also as a result of this lower symmetry the four main configurations employed are actually completely equivalent to the two corresponding species in the first example.

[d] The $^3A_2$ SCF MO's are used for the high-threshold CI carried out to determine the approximate NO's.

[e] In this case a different representation of the degenerate species in the MO basis has been chosen than in the first four examples. Also in the latter case use of a second main configuration has only an insignificant effect on the final CI results so that these data are completely comparable in this respect to those of the previous examples (see also Footnote [d]).

of the leading configuration are used in the macro-iteration CI; otherwise the normal single-root selection procedure appears to be quite adequate in the high-threshold CI needed in order to obtain the desired approximate natural orbitals for the final CI treatment.

4. Conclusion

The results of the preceding section suggest a very systematic CI procedure which seems to be of equal validity for all types of electronic states. Aside from the AO basis set employed in the calculation (obviously a critical factor) there is really only one other variable quantity in the entire method, namely the set of main configurations which serves as the nucleus of the CI treatment; the choice of these species can simply be based on their importance in the final CI expansion (or rather a preliminary version thereof), and experience has shown that it is generally sufficient to include only configurations with a coefficient of 0.05 or greater in this set. The number of main configurations can be kept to a minimum by employing approximate natural orbitals for the CI treatment, and these in turn can be obtained quite simply from corresponding SCF MO's merely by carrying out a relatively small CI employing a large energy cut-off value in the selection process and then following this with diagonalization of the resulting density matrix for the state of interest; experience has shown that further macro-iterations of this type lead to no essential change in the results of the final CI itself. The success of this approach in turn is clearly based on the fact that through configuration selection it becomes quite practical (at least for systems of conventional size) to allow for variable occupation of the entire complement of MO's (or NO's) resulting from a given AO basis.

The entire CI procedure thus consists of a series of four well-defined steps: 1. choice of the set of dominant configurations; 2. determination of a set of approximate NO's for the treatment (if necessary) obtained through the use of a high-threshold CI calculation with a suitable set of starting orbitals; 3. solution of the secular problem at *a series of levels of selection* (as measured by the threshold value T) for all single- and double-excitation species with respect to the set of main configurations[9], and finally 4. calculation of the $E(T\rightarrow 0)$ results at each such threshold value (using the ΔE_r data of the neglected configurations) with subsequent extrapolation of these results to zero threshold to obtain the final CI energy $E(0)$. While the $E(T\rightarrow 0)$ values are in general not in complete agreement, their extrapolation to the desired $E(0)$ result seems easily accomplishable to within an error of 5.0×10^{-4} hartree (roughly 0.01 eV), well inside the accuracy range normally required for meaningful comparison with experimental results.

In summary the individualized selection process greatly reduces the amount of computation in a given CI problem by systematically excluding a substantial number of weakly interacting configurations from the final secular equation actually to be solved, while at the same time affording a sound basis upon which

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[9] Where of course only the matrix elements for the lowest T value (typically 20 μh) have to be specifically evaluated, and at the same time the resulting eigenvector of the larger secular equation can be used very efficiently as a starting vector for the higher threshold cases.

to accurately estimate the results of the treatment in which all such neglected species are given full consideration. Such procedures also effectively remove most of the uncertainty involved in the choice of an MO basis in the CI by affording the use of larger valence sets than would otherwise be possible and also by enabling what amounts to a non-iterative method for realization of the most efficient transformation of the orbitals for use in the calculations. Furthermore, since the number of main configurations on which such treatments are ultimately based is usually not large (generally no more than five and often as few as one or two), there is in fact little more ambiguity involved in these calculations than in those of the much more restrictive SCF method, with its completely uncorrelated wavefunction. Given this fact plus the existence of large classes of chemical and physical problems for which correlation effects play a dominant role it seems clear that the increased practicability afforded to CI studies because of configuration selection techniques will be of considerable value in future theoretical investigations.

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