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Energy Extrapolation in CI Calculations*

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A method of extrapolating the CI energy of large configuration subspaces is discussed and illustrated in a series of examples. Secular equations for selected groups of configurations are solved, while the influence of the remaining elements in the subspace is accounted for in a statistical manner. Criteria for judging the reliability of the extrapolation technique are developed and evidence is presented underscoring the need to go beyond the level of truncated CI calculations in obtaining excitation energy and potential surface results.

Key words: CI methods, energy extrapolation in ~

1. Introduction

The practicability of the configuration interaction (or mixing) method of obtaining electronic wavefunctions is limited by the fact that (generally speaking) the size of the secular problems which arise from such treatments increases in a factorial manner with the number of AO functions in the basis set employed. For systems of even moderate size the direct solution of the matrix corresponding to a full CI seems far out of reach at present, but this fact in itself does not foreclose the possibility of using such techniques to make predictions of chemical and physical phenomena, provided a well-defined procedure for choosing a *subspace* of the full configuration set can be developed which allows an essentially equivalent treatment of each of the electronic states of interest for all nuclear conformations.

In an orthogonal basis early attempts to accomplish such a division of the total configuration space have generally centered on the fact that only singly- and doubly-excited species can interact *directly* with the leading configuration of a given electronic state [1, 2]. On the other hand some triple and quadruple (and even higher-order) excitations relative to the leading term have been found to be important [3–7] in CI expansions as a result of *direct interaction* with *other* terms in the CI wavefunction which themselves are related to the leading species by only a double (or single) excitation. Including all single- and double-excitation species relative to a *series* of the most important terms in a given CI expansion brings in the *key triply- and quadruply-excited species* (in the earlier notation) *in a quite selective manner.*

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The fact remains, however, that even such double-excitation subspaces generally comprise many more configurations than can be handled conveniently *by direct solution* of the corresponding secular problem. It has been shown earlier [7–9] that the energy-lowering capability of the individual configurations in the subspace can be tested effectively on the basis of their Hamiltonian matrix elements with each of the generating (or reference) configurations, thereby also providing a satisfactory means of *selecting* only the most important species for inclusion in a truncated CI calculation. In addition there is an indication [7] that the information contained in such estimated energy lowerings is sufficient to allow one to extrapolate the results of the truncated CI calculations back to zero selection-threshold, i.e. to the eigenvalue which results from the solution of the secular problem for the *entire generated subspace*. The present paper examines the proposed selection-extrapolation technique by considering a series of applications for various molecular systems. Criteria are developed for judging the reliability of such extrapolation techniques, and at the same time evidence is presented to demonstrate that failure to go beyond the level of *a truncated* CI *within the generated double-excitation subspace* can introduce significant errors in the final results of the treatment.

2. Theoretical Aspects of the Energy Extrapolation Technique

In principle it is possible to associate with each configuration φ_i in a given space a quantity ΔE_i which represents the energy lowering capability of this species upon inclusion in the CI matrix. By choosing an energy cut-off value T (selection threshold) with which to compare such results it is possible to construct a truncated secular matrix in which only those configurations are included which possess a ΔE_i value greater than this amount. Because of the variation principle the CI energy E is necessarily a monotonically increasing function of T; similarly the quantity

$$\Delta E_r(T) \equiv E(T=0) - E(T) \tag{1}$$

is a monotonically decreasing function. A plot of the family of quantities

$$E_\lambda(T) = E(T) + \lambda \Delta E_r(T), \tag{2}$$

where λ is an arbitrary constant, is shown in Fig. 1 for the case in which the zero-threshold energy is available. By construction the curve for $\lambda = 1$ is a constant with value equal to $E(0)$, while because of the properties of $\Delta E_r(T)$ it follows that all of the other species in the figure are either monotonically increasing ($\lambda < 1.0$, including $E(T)$ itself of course) or monotonically decreasing ($\lambda > 1.0$). In addition each of the E_λ curves approaches the same limit at $T=0$, namely $E(0)$, because of the fact that at that point ΔE_r necessarily vanishes since no species are then omitted from the CI.

If the exact quantity $\Delta E_r(T)$ is not known it is possible to proceed by employing the approximate quantity

$$\widetilde{\Delta E}_r(T) = \sum \widetilde{\Delta E}_i(T), \tag{3}$$

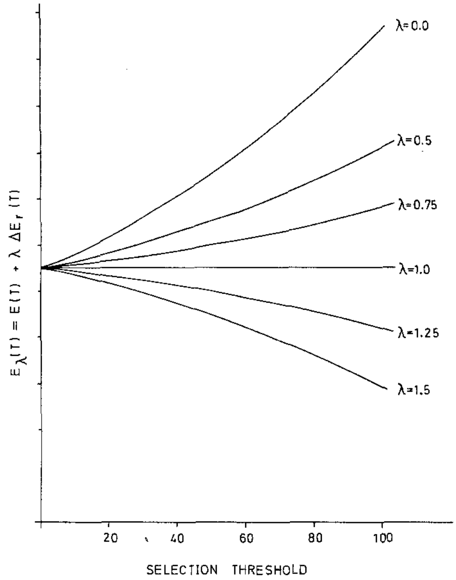

Fig. 1. Family of E_λ curves as defined in Eq. (2) plotted as a function of the selection threshold T

where the sum is taken over all those configurations in the generated subspace which are not included in the secular problem at a given value of T. In the present work the $\widetilde{\Delta E}_i$ values are obtained as the energy lowerings which result upon adding the corresponding test species to the original set of generating (reference) configurations [7]; other definitions for similar quantities used in selection procedures may be found elsewhere [8, 9, 10].

Despite its approximate nature the sum quantity in Eq. (3) still has several characteristics in common with the exact $\Delta E_r(T)$ introduced in Eq. (1), namely it decreases monotonically with T and vanishes at zero threshold. If a sufficiently large group of reference configurations were to be employed in the test secular equations the $\widetilde{\Delta E}_i$ results could approach their exact values, but in practice such a situation is not conveniently realized and, more importantly, it is apparently not necessary that it be achieved in order to obtain a good estimation of the desired $E(0)$ result. Because of the properties of $\widetilde{\Delta E}_r(T)$ it still follows that the family of E_λ curves obtained by substituting this approximate quantity for the true $\Delta E_r(T)$ species (hereafter denoted as $\tilde{E}_\lambda$) converges to a common limit $E(0)$. If the pattern of convergence is smooth enough upon using the calculated $\widetilde{\Delta E}_i$ values to obtain an estimate for $\Delta E_r(T)$, it follows that the desired zero-threshold energy value can be obtained to good accuracy without the explicit solution of secular equations *beyond a certain minimum threshold value.*

3. Examples

A plot of the appropriate energy quantities used in the extrapolation procedure for several states of water is given in Fig. 2; details of the AO basis and configuration sets employed may be found in the original Ref. [11]. Explicit secular equations

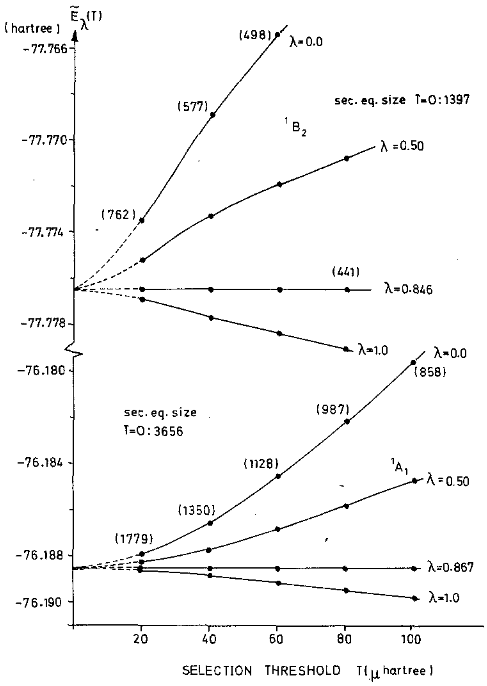

Fig. 2. Comparison of the pattern of $\tilde{E}_\lambda$ curves for the ground and $^1B_2$ excited states of H_2O. The sizes of the secular equations actually solved for a given T value are given in parentheses

for threshold values of T = 20, 40, 60, 80 and 100 μ hartree respectively have been carried out for each state; the corresponding secular equation sizes are given in parentheses at the respective $E(T)$ point in each case, while the size of the entire double-excitation subspace is also indicated in the figure (the same format is used throughout this paper). Despite the fact that the curve for the theoretical value of $\lambda = 1.0$ is not a constant in either case, it still seems clear from the general smoothness (and monotonicity) of the various $\tilde{E}_\lambda$ curves and their overall pattern of convergence that the true $E(0)$ values can be determined to quite good accuracy from these results. The curves for $\lambda = 0.846$ ($^1B_2$) and $\lambda = 0.867$ ($^1A_1$) are very nearly constant and there appears little question that they remain so beyond $T = 20$ μhartree, coming to a common point with the other $\tilde{E}_\lambda$ species at zero threshold.

Similar behavior has been observed for a number of other states of water in which the *untruncated* CI *has been carried through explicitly*, a typical example of which ($^3B_2$ state) is given in Fig. 3. No unusual changes in the slope of the various $\tilde{E}_\lambda$ curves are observed at lower threshold values and a roughly constant curve is found for $\lambda = 0.838$. Judging from the latter species alone one would have estimated $E(0)$ in this case to be -75.7847 hartree based on the calculations at only $T = 40$, 60 and 80 μhartree; this value represents an error of roughly 2×10^{-4} hartree, even though the order of the largest secular equation solved is only 777, less than 40% of the total subspace. The estimated $\widetilde{\Delta E}_r$ ($T = 40$) value

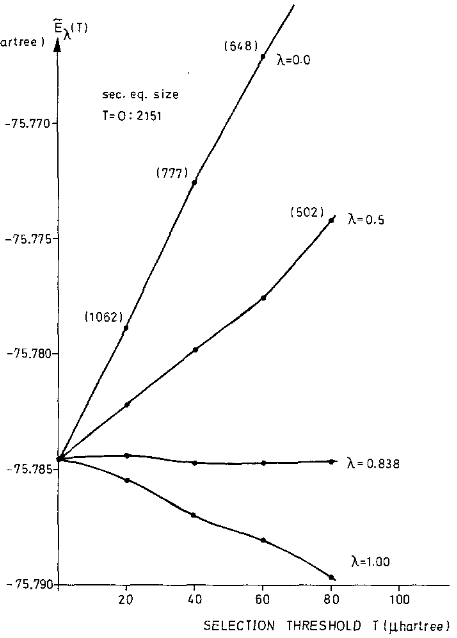

Fig. 3. Family of $E_\lambda(T)$ curves as a function of the selection threshold for the $^3B_2$ state of water. The secular equation for $T=0$ has been solved explicitly

is 0.0145 hartree so that the extrapolation from this point would be accurate to within roughly 1% of the remainder term. The significance of the optimum λ value in each case is clear, namely as the adjustment parameter needed to correct for the errors in the *average* $\widetilde{\Delta E}_i$ value estimated from the secular equation results. The most poignant observation to be made from the results of Figs. 2–3 in comparison to those for the ideal situation given in Fig. 1 is that it is not at all necessary that the $\sum\widetilde{\Delta E}_i$ results be obtained to high *absolute* accuracy, i.e. that constancy be obtained exactly for the theoretical value of $\lambda=1.0$, in order to accomplish the extrapolation to satisfactory accuracy.

For larger configuration sets in which it becomes inconvenient (if possible at all) to solve the CI for the entire subspace one can still check on the consistency of the extrapolated results by comparing estimates of $E(0)$ based on several threshold ranges. For the $^3\Sigma_g^-$ ground state of O_2, for example, calculations have been carried out for both the 20 to 100 μhartree threshold range and also that between 5 and 25 μhartree (two reference configurations, double-zeta plus *s*, *pπ* and *dπ* bond functions in the basis) [12]. The results plotted in Figs. 4a–b respectively both indicate an $E(0)$ value of roughly -149.8950 hartree, with the uncertainty being only somewhat smaller in the lower threshold range calculation. Again no unusual changes in the slopes of the various $\tilde{E}_\lambda$ curves are observed as the value of T is decreased, and a very nearly constant species is observed in each figure, for $\lambda=0.63$–0.65. The fact that the constant-energy λ value is lower in this case than in any of the foregoing H_2O examples would only seem to indicate something about the *absolute accuracy* of the calculated $\widetilde{\Delta E}_r$ compared to the exact ΔE_r values

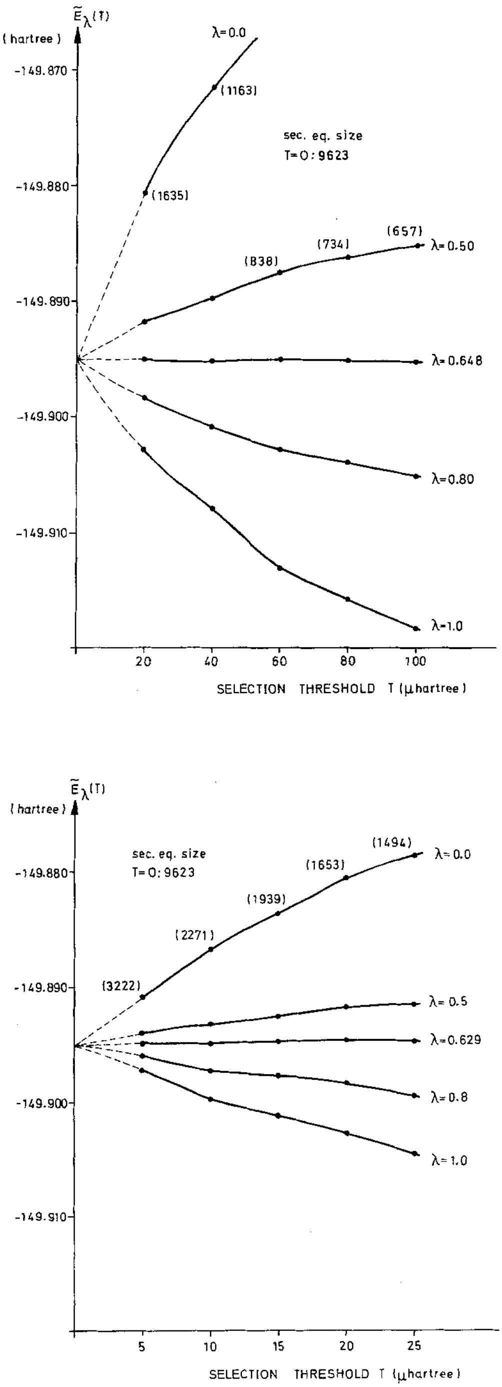

Fig. 4. Family of $\tilde{E}_\lambda(T)$ curves for the ground state of O_2 as a function of the selection threshold from $T=0$ to 100 μ hartree (Fig. a) and from $T=0$ to 25 μ hartree (Fig. b). Note the change in abscissa in the two graphs

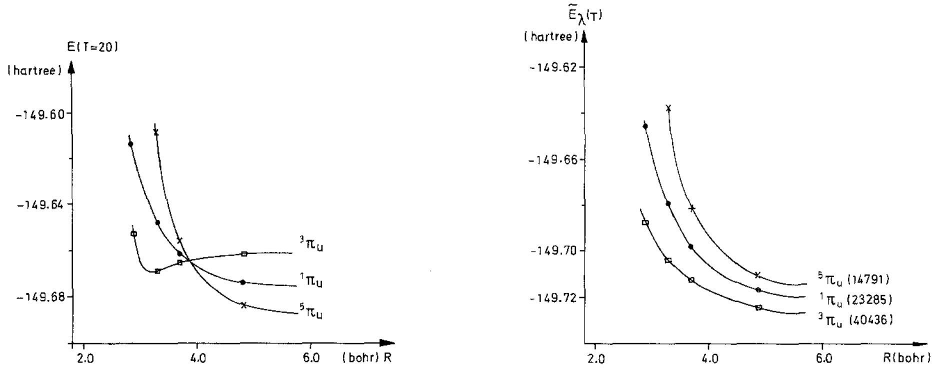

Fig. 5. Potential curves for the $^{5,3,1}\pi_u$ states of O_2 obtained from a CI calculation at selection threshold $T=20$ μhartree (Fig. a) and extrapolated to zero threshold (Fig. b)

in the two types of calculations, and not particularly anything substantive about the behavior of the extrapolation procedure in general.

Many other examples of the presently outlined extrapolation procedure could be given to further illustrate the general points set forth in this section. In calculations for ethane [13] and diborane [14] configuration subspaces of order 40 000 or more have been treated in this manner. Taken as a whole these results indicate that such an extrapolation scheme is capable of obtaining the desired E(0) eigenvalue to quite useful accuracy without necessitating the explicit solution of impractically large secular problems.

Furthermore since it has been found that the pattern of the $E(T)$ secular equation results ($\lambda=0.0$ curve) can vary significantly with the nature of both the electronic state and the associated nuclear conformation, it seems quite important in general to go beyond the level of a truncated CI treatment. In the case of the $^1B_2-{}^1A_1$ transition in water, for example, it is obvious from Fig. 2 that the calculated excitation energy is not at all independent of the value of the threshold T used in selecting the configurations for inclusion in a given secular equation. Analogous results for other systems such as ethane [13] and diimide [15] demonstrate the same point. Nor are potential curves calculated with truncated CI results necessarily found to be satisfactory substitutes for data obtained when the entire configuration subspace is considered, as is clearly illustrated by calculations for the $^{5,3,1}\pi_u$ states of O_2 (Figs. 5a–b). The potential curves resulting from a CI at a relatively small selection threshold of $T=20$ μhartree are seen to be markedly different from the corresponding species obtained by extrapolation to zero threshold in each case. In fact for large R values the order of the three states is actually inverted in the truncated ($T=20$ μhartree) CI, despite the fact that even single-configuration treatments find that the triplet state is the most stable of the three.

4. Observed Characteristics of the Extrapolation Method

From numerous applications of the extrapolation method to a variety of systems a number of characteristics of the general technique can be observed.

The choice of AO basis set appears to have only a minimal effect on the operation of the extrapolation procedure *per se*, at least judging from data obtained for various states of ethylene [7, 16] and water [11] in essentially double-zeta bases with and without polarization species. Increasing the number of AO's necessarily leads to an enlarged configuration subspace, but the shapes of the resulting $\tilde{E}_\lambda$ curves have not been found to be any less smooth nor has their convergence pattern to zero threshold seemingly been impaired by such improvements in the overall theoretical treatment.

Use of natural orbitals in constructing the various configurations for a given state also does not appear to cause any significant change in the operation of the extrapolation technique, although it generally does tend to concentrate the energy-lowering capacity in a smaller number of configurations than is otherwise possible. If a sufficiently large number of reference configurations is used to generate the single- and double-excitation space in a given CI treatment, however, there is only a relatively small advantage in using NO's to construct the requisite determinantal basis, at least as long as the energy extrapolation to zero threshold is actually carried out [7].

Increasing the number of generating configurations likewise seems to have little influence on the extrapolation pattern itself. In this case the size of the configuration subset becomes very much larger (in a $S\Sigma_g^-$ calculation, for example, the secular equation size increases from 9623 to 39386 upon introduction of four new main configurations to a previous reference set of two) but nevertheless it is found that the secular equation sizes at a given value of T (for which explicit calculations might be carried out) in general change very little as long as the additional reference species appear with only moderately large expansion coefficients ($|c_i| < 0.20$, for example). From a practical point of view this result means that only the time required to accomplish the configuration selection is really increased while the construction and solution of the various secular equations at finite T require virtually no additional effort over that necessary in the treatment with a smaller set of generating species[1]. In general the λ value corresponding to the constant energy curve is more nearly equal to unity in the treatment with more generating configurations (it increases from 0.62 to 0.75 in the $^3\Sigma_g^-$ calculation in going from two to six reference species, for example), thereby indicating that the absolute accuracy of the test energy lowerings $\widetilde{\Delta E}_i$ is improved upon this change in the selection procedure.

There is some indication that the accuracy of the extrapolation procedure suffers somewhat when a *number* of configurations of *roughly equal importance* present themselves in the expansion of a given wavefunction, as occurs for example in dissociative regions of the potential surfaces in cases for which the Hartree-Fock approximation is very poor. An example of such behavior occurs for the $^1\pi_u$ state of O_2 at $R = 10.0$ bohr; in an MO basis six configurations of equal (or nearly equal) importance are required to represent the simplest dissociation limit (^3P) of the corresponding atomic state. For such dissociative species it is quite

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[1] Nevertheless in order to obtain a meaningful statistical sample for evaluating the effect of the newly added reference configurations it is often necessary to employ somewhat smaller values of the selection threshold T, thereby causing a further increase in the size of the computational problem.

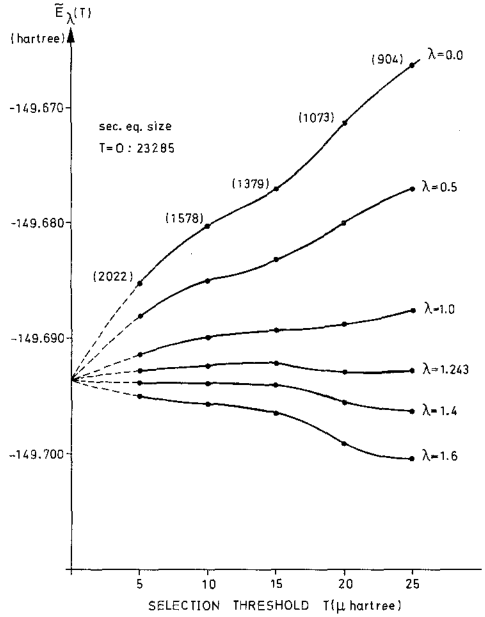

Fig. 6a. Family of $\tilde{E}_\lambda$ curves for the ${}^1\pi_u$ state of O_2 at $R = 10$ bohr as a function of the selection threshold

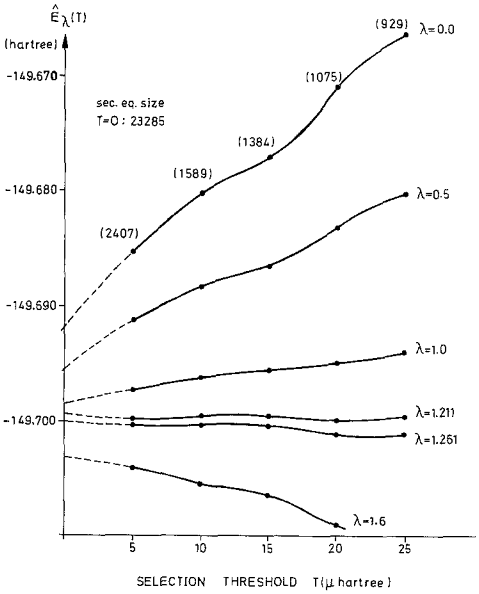

Fig. 6b. Family of $\hat{E}_\lambda$ curves for the ${}^1\pi_u$ state of O_2 at $R = 10$ bohr as a function of the selection threshold. In this case the $\Delta\hat{E}_i$ values are obtained to relatively low accuracy. As a result the family of $\hat{E}_\lambda \equiv E(T) + \lambda\sum\Delta\hat{E}_i$ curves do not converge to a common $E(0)$ value

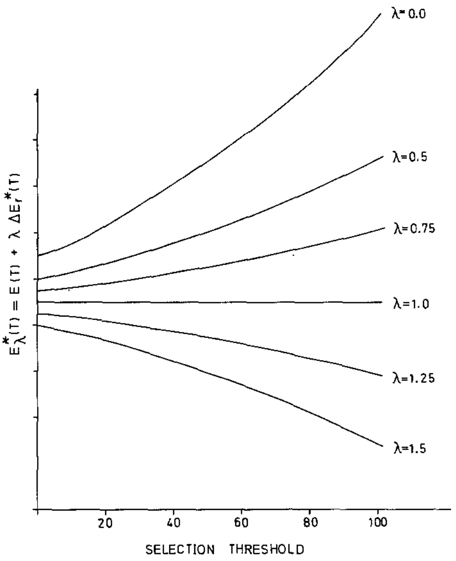

Fig. 7. Theoretical construction of the family of E_λ^* curves in which ΔE_r is in error by a certain amount. For this reason convergence is no longer obtained at $T=0$

often necessary to solve secular equations corresponding to smaller values of T (Fig. 6a) in order to obtain the same accuracy as for a treatment in which a single dominant term appears in the CI expansion[2]. The playoff between accuracy and scope of calculation undertaken is again apparent in this example and is fundamental to the operation of the extrapolation procedure as a whole.

The relatively different circumstances observed in energy extrapolation for O_2 states at large R values raise the question as to whether an incorrect $E(0)$ value might be indicated from an otherwise smooth extrapolation pattern. While the occurrence of an erroneous $E(0)$ estimate cannot be ruled out on theoretical grounds, the evidence available suggests that the group of $\tilde{E}_\lambda$ curves can call attention to such situations should they develop. Consider, for example, the same ${}^1\pi_u$ calculation as before with the exception that all $\widetilde{\Delta E}_i$ values are calculated to smaller accuracy (IBM single precision). At this level $\widetilde{\Delta E}_r$ is calculated to be 0.005 hartree greater (as a result of error accumulation) at $T=5$ μhartree than in the previous (higher precision) case. The corresponding (erroneous) $\hat{E}_\lambda$ curves are displayed in Fig. 6b for comparison with the correct results of Fig. 6a. Although the curves in Fig. 6b show similarly smooth variations as those in Fig. 6a, they do not approach a common point at zero threshold. The reason for this distinction lies clearly in the fact that while an error in $\widetilde{\Delta E}_r$ naturally has no effect on the $\lambda=0$ curve, it has a successively larger influence on the curves with non-zero λ, causing the $\tilde{E}_{(\lambda=1.0)}$ curve to be *displaced downward by essentially the total error* in the $\widetilde{\Delta E}_r$ term (0.005 hartree). The analogous situation clearly also develops in

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[2] On the other hand, even at $T=5$ μ hartree over 90% of the elements in the configuration subspace are still omitted via the selection process, and calculations at still smaller values of T are well within the realm of practicability.

the ideal case when a *constant* error is introduced, as can be seen from a comparison of Fig. 7 with Fig. 1. *The shapes for all the component curves are the same* in the two cases *but the spacing between them is altered in direct proportion to the error in* ΔE_r. At the very least these examples demonstrate that the general appearance of the family of $\tilde{E}_\lambda$ curves is very sensitive to the accuracy with which the component $\widetilde{\Delta E}_r$ quantities are determined.

In short experience strongly indicates that the $\tilde{E}_\lambda$ curves (as defined in the present work) approach a common point at zero threshold in a smooth manner with a nearly constant member occurring at roughly the correct limit for $E(0)$. This result in turn simply implies that on an averaged basis the proportionality between estimated (through the test secular equation results) and true ΔE_i values remains fairly constant in the range of T for which configuration selection is usually carried out (1 to 100 μhartree, in general). Whether a similar constant proportionality factor is characteristic of other types of energy lowering estimating procedures (such as those involving Shavitt's B_k approximation [10] or perturbation methods [8, 9]) remains to be tested but the likelihood is that such changes in the overall technique are not of substantive importance in this regard, since the same information (namely matrix elements between the test and reference species) is being employed in each instance.

5. Conclusion

The present extrapolation method allows one to obtain the CI energy for the entire single- and double-excitation subspace (w.r.t. one or more reference configurations) by solving a series of moderately large secular equations in which the more weakly interacting species are not explicitly included, but in which their effect on the final results is taken into account by essentially statistical means. The reliability with which the energy extrapolation is accomplished can be judged internally from the appearance of the $\tilde{E}_\lambda$ curves, particularly on the basis of how well the family of curves converges to a common point at zero threshold and how closely they approach the ideal situation depicted in Fig. 1, in which an arbitrary weighting of the correction term ΔE_r leads to universally monotonic behavior.

The overall accuracy of this technique depends on the value of $\widetilde{\Delta E}_r$, i.e. the sum of the individual $\widetilde{\Delta E}_i$ values, which is calculated at the *smallest* energy threshold T for which explicit solution of a secular equation is carried through. Experience indicates that the CI energy $E(0)$ for the entire configuration subspace can generally be extrapolated to within an error of approximately 5% of the foregoing quantity, which is to say that for every 0.01 hartree in $\widetilde{\Delta E}_r$ itself an error of roughly 0.01 eV can be expected in the end result for $E(0)$. Generally speaking a value for $|\Delta E_r|$ in the order of 0.01 hartree is reached before as many as 10% of the elements of the total subspace are included in the secular equations actually to be solved in the extrapolation procedure. Taken together such results insure a high level of practicability for CI methods which make use of this technique.

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