THEORETICA CHIMICA ACTA

Theoret. Chim. Acta (Berl.) 62, 163–174 (1982)

On the Size Consistence of a Few Approximate Multireference CI Schemes

Jean-Paul Malrieu

Laboratoire de Physique Quantique (E.R.A. 821) Inversité Paul Sabatier, 118, route de Narbonne 31062 Toulouse Cedex (France)

Using the canonical problem of N separate electron pairs, the N dependence of approximate multireference CI schemes is analyzed. When the DCI is taken as multireference space, the second order Quasi Degenerate Many Body Perturbation Theory (QD(MB)PT) gives twice the expected correction, while the CIPSI algorithm gives 66% of it, and the MRDCI a vanishing part of it. A modified QDPT effective hamiltonian, and a combination of CIPSI and QDPT algorithms seem to give better trends.

Key words: Configuration interaction – Perturbation theory – Manybody problem.

1. Introduction

From the very beginning of its development, the Many Body Perturbation Theory (MBPT) [1] insisted on the N-dependance of the various treatments of the correlation problem. The rejection of the Brillouin–Wigner approach [1] was based on this criterion while the linked cluster theorem [2] allowed understanding of the success of the Rayleigh Schrödinger expansion. The failure of the CI truncation to the doubly excited determinants (DCI) was clearly understood as due to the normalization of the wave function; this normalization introduces some unlinked contributions which would be cancelled by the unlinked contributions involving the quadruple (or higher) excitations. To avoid the normalization defect, Davidson [3, 4] proposed therefore an approximate correction for the correlation energy $\varepsilon_{\text{corr}}$,

$$\varepsilon_{\text{corr}} = \varepsilon_{\text{DCI}}(2 - c_0^2) \tag{1}$$

0040-5744/82/0062/0163/$02.40

later modified by Siegbahn [5]

$$\varepsilon_{\text{corr}} = \varepsilon_{\text{DCI}} \times \frac{1}{c_0^2}, \tag{2}$$

where c_0^2 is the weight of the Ground State determinant in the normalized DCI eigenvector.

During the last ten years various schemes have been proposed to improve the convergence of the CI expansion by starting from multireference (or multi-configurational) wave functions determined by a preliminary CI procedure. The MRDCI (Multireference Double CI) [6] or the CIPSI [7] schemes belong to that category (see also Refs. 8–13). Another class of procedures uses the so-called Quasi Degenerate (Many Body) Perturbation Theory (QDPT) [14, 15] which builds in a perturbative manner an effective Hamiltonian restricted to a finite "model space" of n determinants, the n eigenvalues of which converge to n exact eigenvalues of the total Hamiltonian.

The present paper tries to analyse the N-dependence behaviour of some of these schemes. To do this, we use the canonical model problem previously used for the N-dependence study of the usual single reference expansion [3, 16, 17]. This model problem concerns N independent (non interacting) subsystems; for sake of simplicity, these subsystems are supposed to be (i) identical, (ii) reduced to an electron pair (He atoms or H_2 molecules), (iii) treated in a two MO basis set. The problem is treated using localized MOs (for the N dependence problem in a delocalized approach see Ref. 17). The first part of the paper recalls briefly some well-known results for the single reference expansion, using a convenient trick. This trick will be used in Sect. 2 for multireference or effective Hamiltonian approaches.

2. The Single Reference Approach

In the model problem, the N doubly excited determinants do not interact and have identical energies ΔE, the Ground State energy being taken as conventional zero; the ground state determinant ϕ_0 interacts through identical matrix elements h with all doubly excited determinants ϕ_J. If for each system, one has one occupied MO φ_i and one virtual MO φ_i^*

$$h = \left\langle \varphi_i \varphi_i \left| \frac{1}{r_{12}} \right| \varphi_i^* \varphi_i^* \right\rangle = K_{\varphi_i \varphi_i^*}.$$

The partitioning technique [19] allows one to show that the energy lowering of the ground state

$$\varepsilon_{\text{DCI}}^{\text{corr}} = \frac{\Delta E}{2}\left(1 - \sqrt{1 + N\left(\frac{2h}{\Delta E}\right)^2}\right) \tag{3}$$

behaves as $h\sqrt{N}$ when N tends to infinity. An alternative demonstration consists in introducing an artificial symmetry [3]. The separated molecules may be

supposed to be disposed around a regular circle; this will not change the result and allows to reduce the $(N+1)$ dimensional problem to a 2-dimensional problem since the ground state is totally symmetrical and there is only one totally symmetrical linear combination of doubly excited determinants

$$\phi_D = 1/\sqrt{N}\left(\sum_I \phi_I\right) \tag{4}$$

$$\langle \phi_0 | H | \phi_D \rangle = \sqrt{N} h \tag{5}$$

$$\langle \psi_D | H | \phi_D \rangle = \Delta E. \tag{6}$$

The same pseudo symmetry transformation, may be performed on the $N(N-1)/2$ quadruple configurations, which may be reduced to the totally symmetrical combination (as mentioned by Davidson and Silver [4])

$$\phi_Q = \frac{\sqrt{2}}{\sqrt{N(N-1)}}\left(\sum_{I<J}\sum \phi_{IJ}\right) \tag{7}$$

where ϕ_{IJ} is doubly excited on both I and J subsystems. In the same way the 6-time excited configurations may be combined into

$$\phi_H = \frac{\sqrt{6}}{\sqrt{N(N-1)(N-2)}}\left(\sum_{I<J<K}\sum\sum \phi_{IJK}\right). \tag{8}$$

The full CI matrix may be reduced to a N dimensional matrix the structure of which is pictured in Fig. 1. The detail of the transformation of the off-diagonal element $\langle \phi_D | H | \phi_Q \rangle$ will be given below.

As long as one is interested in the DCI only, it is clear that when N increases, the off-diagonal element of the 2×2 matrix, $\sqrt{N}h$, becomes much larger than ΔE and the stabilization of the ground states becomes $-\sqrt{N}h$, the eigenvector tends to be

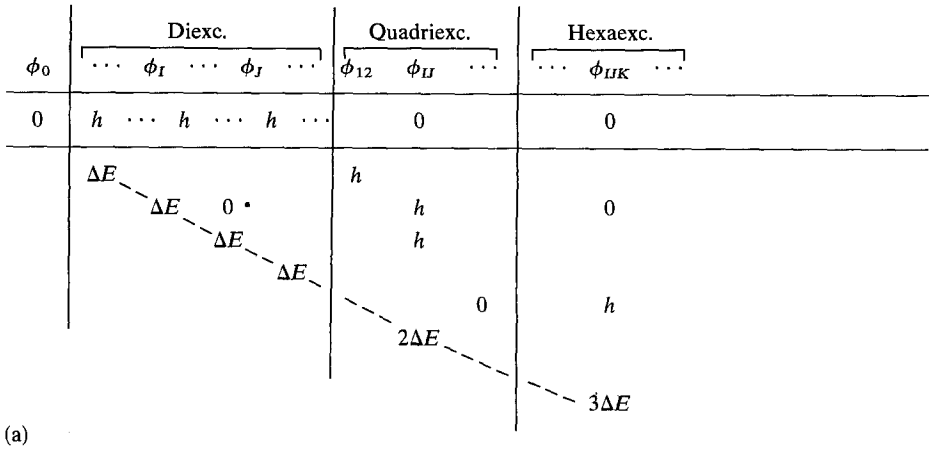
$$\psi_{\mathrm{DCI}} = 1/\sqrt{2}(\phi_0 - \phi_D) = \frac{1}{\sqrt{2}}\left(\phi_0 - \frac{1}{\sqrt{N}}\sum_I \phi_I\right). \tag{9}$$

The eigenvector of the double CI diagonalization tends to have an equal weight on the Ground State determinant and on the doubly excited ones. This result should be compared with the exact solution, which is the product of the solutions for each subsystem

$$\psi = \prod_{i=1,N} (\lambda |\varphi_i \bar{\varphi}_i| + \mu |\varphi_i^* \bar{\varphi}_i^*|) \tag{10}$$

where λ and μ depend on h and ΔE. Developing that wave function on its lowest excitations components gives

$$\begin{aligned} \psi &= \lambda^N \phi_0 + \lambda^{N-1} \mu \left(\sum_I \phi_I\right) + \cdots \\ &= \lambda^{N-1}(\lambda \phi_0 + \mu \sqrt{N} \phi_D) + \cdots . \end{aligned} \tag{11}$$



(a)

ϕ_0	ϕ_D	ϕ_Q	ϕ_H
0	$\sqrt{N}h$	0	0
	ΔE	$\sqrt{2(N-1)}\,h$	0
		$2\Delta E$	$\sqrt{3(N-2)}\,h$
			$3\Delta E$

(b)

Fig. 1. Structure of the CI matrix
(a) in the basis of determinants
(b) after symmetry transformation

Then the component of the exact wave function on ϕ_D, i.e. on the Doubly Excited determinants, is $\sqrt{N}\mu\lambda^{-1}$ times larger than the Ground State determinant component; in terms of weights, it means that the ratio $(\sum_I C_I^2)/C_0^2$ tends to $N(\mu/\lambda)^2$ in the exact solution while it tends to 1 in the DCI solution. The DCI eigenvector overestimates qualitatively the importance of the Ground State determinant with respect to the doubly excited ones.

As explicit in Eq. (9), it becomes clear that c_0^2 tends to $\frac{1}{2}$ when N tends to infinity in the DCI approximation. Then the Davidson's correction will tend to multiply the DCI correlation energy by a factor $\frac{3}{2}$ (cf. Eq. (1)); the Davidson's corrected DCI energy will behave as $-\frac{3}{2}\sqrt{N}h$ instead of the expected $-N(h^2/\Delta E)$ variation [20]. This correction fails to give the correct asymptotic behaviour of the correlation energy. If one goes to the Siegbahn correction, the multiplying factor is equal to 2,

$$\varepsilon_{\text{corr}}^{\text{Siegb}} = -2\sqrt{N}\,h \quad \text{when } N \to \infty.$$

As previously noticed [3, 20] these corrections can only compensate the low order defects, i.e. the effect of the quadruply excited determinants to compensate part of the normalization defect; they cannot insure a satisfactory behaviour of

the energy, since the wave function involves higher and higher levels of excitations. A very simple formula has been proposed later on by Davidson and Silver [3]

$$\varepsilon_{\text{corr}} = \varepsilon_{\text{DCI}}\left(1+\frac{1-c_0^2}{2c_0^2-1}\right) = \varepsilon_{\text{DCI}}\left(\frac{c_0^2}{2c_0^2-1}\right). \tag{12}$$

The behaviour of c_0^2 as a function of N for large N is easy to establish from perturbation theory, starting from rotated wave functions

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_0 - \phi_D), \qquad \psi_2 = \frac{1}{\sqrt{2}}(\phi_0 + \phi_D).$$

The DCI matrix is written as

$$\begin{bmatrix} \frac{\Delta E}{2} - \sqrt{N}h & -\frac{\Delta E}{2} \\ & \frac{\Delta E}{2} + \sqrt{N}h \end{bmatrix}$$

the first-order corrected lowest eigenvector of which is

$$\begin{aligned} \psi &= \frac{1}{\sqrt{2}}(\phi_0 - \phi_D) + \frac{\Delta E}{4\sqrt{2N}h}(\phi_0 + \phi_D) + \cdots \\ c_0 &\simeq \frac{1}{\sqrt{2}}\left(1 + \frac{\Delta E}{4\sqrt{N}h} + \cdots\right) \\ 2c_0^2 &\simeq 1 + \frac{\Delta E}{2\sqrt{N}h} + \cdots \end{aligned} \tag{13}$$

and the corrected correlation energy becomes

$$\varepsilon_{\text{corr}} = -\sqrt{N}h\left(\frac{0.5}{\Delta E/2\sqrt{N}h}\right) = -N\frac{h^2}{\Delta E}$$

which has the right behaviour. One may wonder why formula (12) is not frequently used, while Eq. (1) received hundreds of applications.

3. Multireference Schemes

3.1. CIPSI *with a* DCI *variational zeroth order wave function*

The CIPSI algorithm [7] consists in perturbing a multiconfigurational zeroth order wave function resulting from a preliminary variational CI among the most important determinants for the considered state. In the canonical problem this leads to define the zeroth order wave function on the DCI basis of determinants. For large N,

$$\psi \to 1/\sqrt{2}(\phi_0 - \phi_D),$$

and its zeroth order energy, in the barycenter definition of the unperturbed hamiltonian [7], is the mean value of the diagonal zeroth order hamiltonian in the basis of determinants

$$E_0(\psi_{\mathrm{DCI}}) = \tfrac{1}{2}\langle \phi_0 - \phi_{\mathrm{D}} | H_0 | \phi_0 - \phi_{\mathrm{D}} \rangle \to \frac{\Delta E}{2} \quad \text{when } N \to \infty.$$

The second-order effect of the quadruple excitations on ψ_{DCI} is easily calculated as a sum over the quadruply excited determinants ϕ_{JK}

$$\varepsilon^2 = \frac{1}{2} \sum_{\substack{JK \text{ quadr.} \\ (J<K)}} \frac{\left[\langle \phi_{JK} | H | \phi_0 - \sum_I \phi_I / \sqrt{N} \rangle \right]^2}{\frac{\Delta E}{2} - 2\Delta E}. \tag{14}$$

Each of the $N(N-1)/2$ quadruply excited determinants ϕ_{IJ} interacts with two doubly excited determinants ϕ_I and ϕ_J

$$\langle \phi_{IJ} | H | \psi_{\mathrm{DCI}} \rangle = \frac{\sqrt{2}h}{N}$$

leading to a second order correction $-(2h^2/N\Delta E)(\frac{2}{3})$

The total second order correction is then

$$\varepsilon^{(2)} = N\frac{(N-1)}{2} \times \frac{-2h^2}{N\Delta E}(\tfrac{2}{3}) = -(N-1)\frac{h^2}{\Delta E}(\tfrac{2}{3}). \tag{15}$$

When CIPSI starts from the variational result of the double CI, the first order energy only gives a correction proportional to $\sqrt{N}$, but the second order effect of the quadruple excitations restores the proportionality to the number of particles. However the size inconsistence of the variational wave function results in an underestimation of the correlation; for large N the error reaches *one third* of the correlation energy.

3.2. MRDCI

The MRDCI [6] process is based on the same selection idea as the CIPSI scheme; the zeroth order wave function involves the most important configurations, then all double excitations are performed on this multireference wave function ψ_0 the most important ones are treated variationally, while the small contributions may be treated by 2×2 CIs between ψ_0 and the configuration ϕ_J. In the model problem, the multireference wave function will be the DCI solution and the double excitations will lead to the quadruply excited configurations. If all these quadruple configurations are included in the large CI diagonalization (which the authors consider as the most reliable result), this procedure is equivalent to the

diagonalization of the 3×3 matrix limited to ϕ_0, ϕ_D and ϕ_Q, namely

$$\begin{bmatrix} 0\sqrt{N}h & 0 & \\ \Delta E & \sqrt{2(N-1)}h & \\ & 2\Delta E & \end{bmatrix}.$$

When N is large enough the differences between the diagonal elements are negligible in comparison with the off-diagonal terms, and the lowest solution behaves as $-\sqrt{3N}h$; this procedure will multiply the DCI result by a factor $\sqrt{3}$, intermediate between the Davidson's and Siegbahn's coefficients. The eigenvector of the $(D+Q)$ CI tends to be

$$\psi_{(D+Q)} = \frac{1}{\sqrt{6}}\phi_0 - \frac{1}{\sqrt{2}}\phi_D + \frac{1}{\sqrt{3}}\phi_Q.$$

The relative weight of the gound state tends to diminish in a significant manner.

One may notice that this result is worse than the corresponding "approximate" treatment which sums independently the contribution from all quadruple excitations; when all the quadruple excitations are taken into account through a set of 2×2 CI diagonalizations between ψ_{DCI} and ϕ_{IJ}, one would get $N(N-1)/2$ increments given by the solution of identical 2×2 matrices

$$\begin{matrix} \\ \psi_{\mathrm{DCI}} \\ \phi_{\mathrm{IJ}} \end{matrix} \begin{bmatrix} -\sqrt{N}h & \sqrt{2/N}h \\ & 2\Delta E \end{bmatrix}$$

i.e.

$$\frac{N(N-1)}{2} \times \frac{2h^2}{N} \times \frac{1}{2\Delta E + \sqrt{N}h} \to \sqrt{N}h.$$

This procedure would therefore tend to double the DCI energy lowering i.e. to reach the result of the Siegbahn's correction of the DCI solution which remains a very poor result anyway.

The convergence of the extrapolation procedures of the MRDCI algorithm is therefore very questionnable, since one may consider the inclusion of all double excitations in the Multireference wave function as an already formidable task, the result of which would remain perfectly deceiving for large N. The correction by the first Davidson's correction is not sufficient to insure a consistent behaviour.

3.3. The QDMBPT approach with a DCI model space

The QDMBPT is frequently derived in the complete model space [14] case, i.e. the effective hamiltonian is spanned by all the determinants built from the so called "valence" MOs; here the valence MOs are all the orbitals and the complete model space would be the full CI. Other formalisms [15] allow one to use arbitrary model spaces S, and in our case S might be defined as the Ground State plus all doubly excited determinants. The effective hamiltonian in this basis

will be built by perturbation. To the second order, the matrix elements of this (in principle non-hermitian) operator become

$$H_{IJ}^{\text{eff}\,(2)} = H_{IJ} + \sum_{K \notin S} \frac{\langle I|H|K\rangle\langle K|H|J\rangle}{E_I^0 - E_K^0}. \tag{16}$$

The diagonal terms are perturbed independently by the outside determinants, while off-diagonal terms may appear in H^{eff} between two determinants which interact with the same determinants outside of S. In our case the quadriexcited determinants ϕ_{IJ} which are doubly excited on both I and J will interact with the doubly excited determinants ϕ_I and ϕ_J through a matrix element h.

Any doubly excited determinant ϕ_I interacts with $(N-1)$ quadruply excited determinants $\phi_{IJ} (J \neq I)$ resulting in a second order effective diagonal element

$$H_{II}^{\text{eff}} = \Delta E - (N-1)\frac{h^2}{\Delta E} \tag{17}$$

while each couple of determinants (ϕ_I, ϕ_J) interacts with a quadruply excited determinant ϕ_{IJ}, resulting in

$$\underset{IJ}{H^{\text{eff}}} = -\frac{h^2}{\Delta E} \qquad I \neq J. \tag{18}$$

The effective hamiltonian has equal diagonal elements, and equal off-diagonal elements as shown in Fig. 2. Again one may assume a circular symmetry to reduce the problem to a two-dimensional matrix. But now the energy of the totally symmetric ϕ_D combination of doubly excited determinants is

$$\begin{aligned}\langle \phi_D|H^{\text{eff}}|\phi_D\rangle &= \Delta E - (N-1)\frac{h^2}{\Delta E} + \sum_I \sum_{J \neq I} \frac{1}{N} \langle \phi_I|H^{\text{eff}}|\phi_J\rangle \\ &= \Delta E - 2(N-1)\frac{h^2}{\Delta E}.\end{aligned} \tag{19}$$

$\langle \phi_D|H|\phi_0\rangle$ remains unchanged, equal to $\sqrt{N}h$, but the value of diagonal matrix element of ϕ_D is now decreasing rapidly, so that the asymptotic behaviour of the solutions are the following:

– the lowest eigenfunction tends to concentrate on ϕ_D, i.e. on the doubly excited determinants as desired from Eq. (11). The QDMBPT actually does not suffer the defect of the DCI as regard the wave function; this is expected since after convergence the QDMBPT effective hamiltonians must give the components of the exact wave function on the model space.

– the energy tends to be $-2(N-1)(h^2/\Delta E)$, i.e. to be proportional to N, as desired, but this energy is twice larger than what one would like. While the DCI tends to give a -100% error on the correlation energy, (i.e. a $N^{-1/2}$ decreasing fraction of the correlation energy per electron), the QDMBPT applied to the same model space gives a $+100\%$ error (i.e. makes it twice too large).

ϕ_0	ϕ_1	ϕ_2	$\cdots$	ϕ_I	$\cdots$	ϕ_N
0	h	h	$\cdots$	h	$\cdots$	h
	$\Delta E - \frac{(N-1)h^2}{\Delta E}$	$-\frac{h^2}{\Delta E}$	$\cdots$	$-\frac{h^2}{\Delta E}$	$\cdots$	$-\frac{h^2}{\Delta E}$
		$\Delta E - \frac{(N-1)h^2}{\Delta E}$	$\cdots$	$-\frac{h^2}{\Delta E}$	$\cdots$	$-\frac{h^2}{\Delta E}$
			$\ddots$	$\Delta E - \frac{(N-1)h^2}{\Delta E}$		

Fig. 2. Structure of the QDMBPT second order effective Hamiltonian limited to the DCI model space

This defect may be understood from the fact that the effective hamiltonian tries to give a correct answer not only for the ground state, but also for all the doubly excited states, the mean energy of which actually is $\Delta E - (n-1)(h^2/\Delta E)$. The QDMBPT deals with n_S eigenvectors and eigenvalues if n_S is the dimension of the model space.

3.4. *Correct trends from "Shifted QD(MB)PT" and from* $\langle \psi_{\mathrm{DCI}} | H^{\mathrm{eff}} | \psi_{\mathrm{DCI}} \rangle$

Instead of defining H_0 as the diagonal part of H, one might have taken the model space as degenerate at the zeroth order level, with a zeroth order eigenvalue equal to the ground state zeroth order energy (i.e. our conventional zero); the doubly excited zeroth order energies are shifted to zero

$$H_0 \phi_I = 0 \times \phi_I$$

which means that $\langle \phi_I | V | \phi_I \rangle = \Delta E$

Then the second order effective hamiltonian restricted to the DCI model space takes a different form since the second order corrections resulting from the coupling between double and quadruple excitations are reduced by a factor 2. The effective second order corrected matrix becomes

$$H'^{\mathrm{eff}(1+2)} = \begin{vmatrix} 0 & h & \cdots & h \\ & \left[\Delta E - (N-1)\frac{h^2}{2\Delta E}\right] & -\frac{h^2}{2\Delta E} \cdots & \frac{-h}{2\Delta E} \\ & & \ddots & \\ & & & \left[\Delta E - (N-1)\frac{h^2}{2\Delta E}\right]. \end{vmatrix} \quad (20)$$

The perturbative corrections by the quadruple excitations are one half of those previously obtained in the QDMBPT approach. The transformation into a 2×2 matrix

$$\begin{vmatrix} 0 & \sqrt{N}h \\ \Delta E - (N-1)\frac{h^2}{\Delta E} & \end{vmatrix}$$

shows that the ground state wave function is essentially located on the doubly excited determinants with an energy proportional to $-N(h^2/\Delta E)$.

This result is satisfactory, and it was already obtained by Davidson [21] through a somewhat different approach, consisting in applying the partitioning technique [19] in a modified "energy-independent B_K" approach to "dress" the doubly excited configurations by their interaction with the quadruple excitations (cf. also Ref. 22). We think that the present QDPT approach is more direct. It tends to suggest that the direct application of the QDPT may lead to a poor convergence and that, as long as one is interested in a single eigenstate it might be worthwhile to introduce some specific effective Hamiltonians essentially suited for the search of this peculiar eigenstate, the lowest orders giving more reliable results than the standard technique which is supposed to deal with n eigenstates simultaneously.

A satisfactory result is also obtained from a modified CIPSI algorithm in which one would build the effective Hamiltonian in the model space, in a classical manner, but where one would take the mean value of this effective hamiltonian on the variational wave function resulting from the diagonalization of H in the model space S. If S is the model space

$$P_S = \sum_{K \in S} |K\rangle\langle K|$$

$$P_S H P_S \psi_0 = E_m^0 \psi_0$$

for

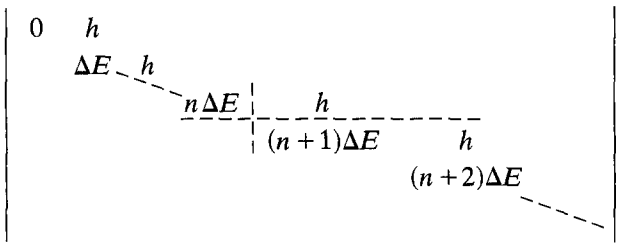
$$K, L_{\in S}, \langle K|H^{\text{eff}(2)}|L\rangle = \sum_{I \notin S} \frac{\langle K|H|I\rangle\langle I|H|L\rangle}{E_K^0 - E_I^0}$$

$$\varepsilon^3 = \langle \psi^0|H^{\text{eff}(2)}|\psi_0\rangle.$$

In our model problem, ψ_0 would be the DCI solution ψ_{DCI}. Turning back to Eq. (9), (16) and (17), it is clear that

$$\langle \psi_{\text{DCI}}|H^{\text{eff}(2)}|\psi_{\text{DCI}}\rangle \simeq -N\frac{h^2}{\Delta E} \tag{21}$$

It is well-known that QDPT may have a poor convergence, due to the "intruder states" problem [14c, 23]. As a typical example one may imagine [7b] CI matrices of the type



where it is impossible to define a reasonable border between the model space and the outside space when the ratio $h/\Delta E$ becomes large; the perturbation of the nth line becomes divergent and the diagonalization of H^{eff} will lead to unreliable results, the effective diagonal energies of the lowest right corner becoming too low. If one uses the previously suggested procedure, the variational ψ_0 has small components on these determinants and the mean value of ψ_0 on H^{eff} remains reliable when the perturbation expansion begins to diverge. This combination of CIPSI and QDPT approaches will be explored later on.

4. Conclusion

The poor behaviour of the DCI result does not concern only the energy. The wave function is basically wrong since it overestimates grossly the weight of the ground state determinant with respect to the doubly excited determinants. This defect on the wave function makes the original Davidson's or Siebahn's corrections unable to correct the energy defect of the DCI approximation. The CIPSI algorithm when applied to the DCI wave function restores a N proportional correlation energy, but one third of it is still lacking. The Quasi Degenerate Many Body Perturbation Theory when applied to a model space limited to the DCI basis set also gives a N-proportional correlation energy but twice too large. Two multireference procedures seem to give correct N dependence; one is a "shifted" QDPT effective Hamiltonian, identical to the "energy independent B_K approximation" already suggested by Davidson; the other one is a combination of CIPSI and QDPT algorithms. However the research of a perturbative size consistent multiconfigurational approach to the CI problem still requires some progress.

Acknowledgements. Thanks are due to Prof. E. Davidson for stimulating discussions during the NRCC workshop on Perturbation Theory.

References

1. Brueckner, V. A.: The many body problem. New York: Wiley 1959
2. Goldstone, J.: Proc. R. Soc. **A239**, 267 (1959)
3. a. Davidson, E. R.: The world of quantum chemistry. Daudel, R. Pullman, B. (eds.). Dordrecht: Reidel 1974; b. Langhoff, S. R., Davidson, E. R.: Int. J. Quant. Chem. **8**, 61 (1974)
4. Davidson, E. R., Silver, D. W.: Chem. Phys. Letters **52**, 403 (1977).
5. Siegbahn, P. E. M.: Chem. Phys. Letters **55**, 386 (1978)
6. Buenker, R. J.: Peyerimhoff, S. D.: Theoret. Chim. Acta (Berl.) **12**, 183 (1968); ibidem, **35**, 33 (1974); ibidem, **39**, 217 (1975) Buenker, R. J., Peyerimhoff, S. D., Butscher, W.: Mol. Phys. **35**, 771 (1978)
7. a. Huron, B., Malrieu, J. P., Rancurel, P.: J. Chem. Phys. **58**, 5745 (1973); b. Daudey, J. P., Malrieu, J. P.: Modern trends of quantum chemistry. Carbo (ed.), (to be published)
8. Davidson, E. R., Bender, C. F.: Chem. Phys. Letters, **59**, 369 (1978)
9. Whitten, J. L., Hackenmayer, M.: J. Chem. Phys. **51**, 5584 (1969)
10. Gershgorn, Z., Shavitt, I.: Int. J. Quant. Chem. **2**, 751 (1968).
11. Raseev, G.: Chem. Phys. Letters, **47**, 36 (1977).

12. Siegbahn, P. E. M.: Int. J. Quant. Chem. **18**, 1229 (1980)
13. Bendazzoli, G. L., Fano, G., Ortolani, F., Palmieri, P.: (to be published)
14. a. Van Vleck, J. H.: Phys. Rev. **33**, 467 (1929); b. des Cloizeaux, J.: Nucl. Phys. **20**, 321 (1960; c. Brandow, B. M.: Rev. Mod. Phys. **39**, 771 (1967); d. Shavitt, I., Redmon, T. L.: J. Chem. Phys. **73**, 5711 (1980).
15. Hose, G., Kaldor, U.: J. Phys. **B12**, 3827 (1979)
16. Meunier, A., Levy, B., Berthier, G.: Int. J. Quant. Chem. **10**, 1061 (1976); Kutzelnigg, W., Meunier, A., Levy, B., Berthier, G.: Int. J. Quant. Chem. **12**, 777 (1977); Malrieu, J. P.: Application des techniques de théorie des champs au problème à N corps. Lecture notes. Paris 1970; Malrieu, J. P., Maynau, D.: J. Chim. Phys. **75**, 31 (1978); Meunier, A., Levy, B.: Int. J. Quant. Chem. **16**, 953 (1979)
17. Malrieu, J. P.: J. Chem. Phys. **70**, 4405 (1979)
18. Ruttink, P. J. A.: Chem. Phys. Letters **79**, 253 (1981)
19. Löwdin, P. O.: J. Chem. Phys. **19**, 1396 (1951); J. Mol. Spectrosc. **10**, 12 (1963)
20. Pople, J. A., Sieger, R., Krishman, K.: Int. J. Quant. Chem. **11S**, 149 (1977)
21. Nitzsche, L. E., Davidson, E. R.: J. Chem. Phys. **68**, 3103 (1978); Nitzsche, L. E., Davidson, E. R.: J. Am. Chem. Soc. **100**, 7201 (1978); Davidson, E. R., McMurchie, L. B., Day, S. J.: J. Chem. Phys. **74**, 5491 (1981)
22. Meyer, W.: J. Chem. Phys., **58**, 1017 (1973), Int. J. Quant. Chem., **5**, 341 (1971)
23. Hegarty, D., Robb, M. A.: Mol. Phys. **37**, 1455 (1979)

Received March 19/May 24, 1982