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A Note on the Treatment of Quadruple Excitations in Configuration Interaction

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Perturbation theory is used to justify the approximation in configuration interaction of the coefficients of quadruple excitations as products of coefficients of double excitations. Corresponding energy expressions are presented and tested in a simple application to the beryllium atom. The ideas are likely to be of most use in connection with large configuration interaction calculations.

Consider a configuration interaction (CI) calculation carried out for a closed shell system using an orthonormal set of orbitals $a, a', a'' \dots b, b' \dots n, n' \dots$, where the Slater determinant

$$\Phi_0 = |a\bar{a}b\bar{b}\dots n\bar{n}| \tag{1}$$

represents a solution of the Hartree-Fock equations (perhaps best transformed to a localized orbital representation) and a', a'', etc. represent a set of excited orbitals chosen to allow the pair of electrons in a to correlate, $b' \dots, n' \dots$ etc. being chosen similarily. The dominant terms in such a configuration interaction consist of double excitations such as[1]

$$\Phi_b^{b'} = |a\bar{a}b'\bar{b}'\dots n\bar{n}| \tag{2}$$

corresponding to independent pair correlations.

However, as has been noted by Sinanoğlu and others [1, 2], the coefficient of some quadruple excitations are not negligible because of the parts of such terms which represent two pairs of electrons correlating independently but simultaneously (unlinked clusters in the language of Sinanoğlu). If this is the only significant cause of quadruple excitations, the coefficients of such excitations are equal to the products of the corresponding double excitations, e.g. the coefficient of

$$\Phi_{ab}^{a'b'} = |a'\bar{a}'b'\bar{b}'\dots n\bar{n}| \tag{3}$$

will be the product of the coefficients of $\Phi_a^{a'}$ and $\Phi_b^{b'}$. This has been found to be the case for the calculations of Watson [4] on Be and Ebbing [5] on LiH.

Since, when the number of electron pairs becomes large, the number of quadruple excitation increases as the square of the number of double excitations, it is of interest to investigate the possibility of allowing for quadruple excitations by estimating their coefficients using the above relationship. The following perturbation theory analysis suggests that this might not be an unreasonable procedure.

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[1] For the sake of simplicity I use a single pair of indices to Φ for the double excitation since single excitations are not considered in this note. Thus $\Phi_b^{b'}$ in the present notation corresponds to $\Phi_{b\bar{b}}^{b'\bar{b}'}$ in the notation of Nesbet [3].

The CI matrix including the quadruple excitations has the following form where $K_{\alpha\beta}$ represents an exchange integral between orbitals α and β.

$$\begin{array}{c|ccccccccc}
 & \Phi_0 & \Phi_a^{a'} & \Phi_a^{a''} & \dots & \Phi_b^{b'} & \dots & \Phi_{ab}^{a'b'} & \Phi_{ab}^{a''b'} & \dots \\
\hline
\Phi_0 & E_0 & K_{aa'} & K_{aa''} & \dots & K_{bb'} & \dots & 0 & 0 & \dots \\
\Phi_a^{a'} & K_{aa'} & E_{a'} & K_{a'a''} & \dots & 0 & \dots & K_{bb'} & 0 & \dots \\
\Phi_a^{a''} & K_{aa''} & K_{a'a''} & E_{a''} & \dots & 0 & \dots & 0 & K_{bb'} & \dots \\
\vdots & \vdots & \vdots & \vdots & & \vdots & & \vdots & \vdots & \\
\Phi_b^{b'} & K_{bb'} & 0 & 0 & \dots & E_{b'} & \dots & K_{aa'} & K_{aa''} & \dots \\
\vdots & \vdots & \vdots & \vdots & & \vdots & & \vdots & \vdots & \\
\Phi_{ab}^{a'b'} & 0 & K_{bb'} & 0 & \dots & K_{aa'} & \dots & E_{a'b'} & K_{a'a''} & \dots \\
\Phi_{ab}^{a''b'} & 0 & 0 & K_{bb'} & \dots & K_{aa''} & \dots & K_{a'a''} & E_{a''b'} & \dots \\
\vdots & \vdots & \vdots & \vdots & & \vdots & & \vdots & \vdots &
\end{array} \tag{4}$$

If the off-diagonal part of the matrix is treated as a perturbation, we obtain the following expressions for the first and second order corrections to Φ_0.

$$\Psi^{(1)} = \sum_{p,p'} \frac{K_{pp'}}{(E_0 - E_{p'})} \Phi_p^{p'} \tag{5}$$

$$\begin{aligned}
\Psi^{(2)} = & \sum_{p,p',p'' \neq p'} \frac{K_{pp''} K_{p''p'}}{(E_0 - E_{p'})(E_0 - E_{p''})} \Phi_p^{p'} \\
& + \sum_{p,p',q > p,q'} \left[\frac{K_{pp'} K_{qq'}}{(E_0 - E_{p'})(E_0 - E_{p'q'})} + \frac{K_{pp'} K_{qq'}}{(E_0 - E_{q'})(E_0 - E_{p'q'})} \right] \Phi_{pq}^{p'q'} \\
= & \sum_{p,p',p'' \neq p'} \frac{K_{pp''} K_{p''p'}}{(E_0 - E_{p'})(E_0 - E_{p''})} \Phi_p^{p'} \\
& + \sum_{p,p',q > p,q'} \frac{K_{pp'} K_{qq'} (2E_0 - E_{p'} - E_{q'})}{(E_0 - E_{p'})(E_0 - E_{q'})(E_0 - E_{p'q'})} \Phi_{pq}^{p'q'} .
\end{aligned} \tag{6}$$

The corresponding expressions obtained from the truncated matrix without quadruple excitations are:

$$\Psi^{(1)} = \sum_{p,p'} \frac{K_{pp'}}{(E_0 - E_{p'})} \Phi_p^{p'} \tag{7}$$

$$\Psi^{(2)} = \sum_{p,p',p'' \neq p'} \frac{K_{pp''} K_{p''p'}}{(E_0 - E_{p'})(E_0 - E_{p''})} \Phi_p^{p'} . \tag{8}$$

Thus the coefficients of the double excitations obtained from the truncated matrix are identical, to second order, with those obtained from the full matrix. If these are used to estimate the coefficients of the quadruple excitations the result for the quadruple excitation part of $\Psi^{(2)}$ is

$$\Psi^{(2)}_{\text{est.}} = \sum_{p,p',q > p,q'} \frac{K_{pp'} K_{qq'}}{(\mathrm{E}_0 - \mathrm{E}_{p'})(\mathrm{E}_0 - \mathrm{E}_{q'})} \Phi_{pq}^{p'q'} + \text{higher order terms} . \tag{9}$$

The coefficients in this expansion differ to second order from those in the correct expansion by factors

$$\frac{2E_0 - E_{p'} - E_{q'}}{E_0 - E_{p'q'}} = 1 + \frac{4(J_{pq} + J_{p'q'} - J_{pq'} - J_{p'q}) - 2(K_{pq} + K_{p'q'} - K_{pq'} - K_{p'q})}{E_0 - E_{p'q'}} \tag{10}$$

so that the difference represents at least a third order term and the result is correct to second order.

In fact, if a localized orbital basis is used, the numerator of the second term in (10) is likely to be small even in comparison with one of the Exchange integrals which form the off-diagonal elements of the CI matrix. The Coulomb part of it, for example, can be written

$$4 \int\int [p^2(1) - p'^2(1)] \, [1/r_{12}] \, [q^2(2) - q'^2(2)] \, d\tau_1 \, d\tau_2$$

which represents the electrostatic intereaction between charge distributions each of zero total charge (and small or zero dipole moment) in different regions of space. No such relationship holds in higher orders of perturbation theory; the third order coefficients of the double excitations, for example, include matrix elements involving the quadruple excitations.

The second order wave function determines the energy to fifth order, so that an appreciable improvement in the energy might be expected if this approximate second order wave function is used. The expression for the contribution of quadruple excitations to the fourth order energy turns out to be rather simple. (There are no contributions in lower orders).

$$E^{(4)} = \sum_{p,p',q \neq p,q'} c_p^{p'2} c_q^{q'} K_{qq'} \, . \tag{11}$$

The fifth order expression is rather less tidy.

$$E^{(5)} = \sum_{p,p',q \neq p,q',q'' \neq q'} c_p^{p'} c_q^{q'} c_q^{q''} K_{q'q''} \left[c_p^{p'} + \frac{K_{qq'}}{(E_0 - E_{p'})} \right] . \tag{12}$$

In the trial application of these formulae described below, the contribution of $E^{(5)}$ is negligible and it may well not be worth evaluating in many cases.

It remains to be considered whether the coefficients to be used in Eqs. (11) and (12) should be the first order ones (5) or the true ones obtained by diagonalization of the truncated C.I. matrix. Since the difference is itself a second order one, there is no obvious reason to prefer one to the other, but the trial application suggests that use of the true coefficient leads to a more accurate result, presumably because at least parts of higher order terms are included.

The suggested procedure, then, is to diagonalize the C.I. matrix using doubly excited configurations only, and to add to the wavefunction so obtained all quadruply excited configurations with coefficients equal to the products of those of the corresponding doubly excited configurations using the resulting wavefunction to evaluate expectation values of any operators of interest. For the particular case of the total energy, the expressions (11) and (12) give the appropriate corrections to the value obtained using double excitations only.

We have, as a simple trial case, applied the expressions to the results of a small very limited C.I. wavefunction obtained, for another purpose, for the beryllium atom [6]. Three optimized excited orbitals $2p$, $3s$ and $3p$ are used and consequently only three double excitations Φ_{2s}^{2p}, Φ_{1s}^{3s} and Φ_{1s}^{3p} are considered. We have carried out the exact calculation with and without inclusion of quadruple excitations so as to compare the estimate given by the present method with the exact values. The results are given in the table which is self-explanatory.

The formulae given so far are all derived on the assumption that a given excited orbital is only used in association with a given ground state orbital. If this restriction is relaxed, it is not clear whether the second term in (10) would be small compared with unity. If it is assumed to be, the formulae become of rather greater complexity as can be seen in Eqs. (13) and (14).

$$\Psi^{(2)} = \sum_{p,q>p,r,s>r} (c_p^r c_q^s + c_p^s c_q^r)\, \Phi_{pq}^{rs} + \text{double excitations}\,. \tag{13}$$

$$E^{(4)} = \sum_{p,q \neq p,r,s \neq r} (c_p^{r2} c_q^s + c_p^r c_p^s c_q^r)\, K_{qs}\,. \tag{14}$$

The expression for $E^{(5)}$ is so awkward as not to be worth presenting.

Table. *Comparison of estimated and exact effects of quadruple excitations in beryllium*

	Exact	Using 1st order $c_p^{p'}$	Using exact $c_p^{p'}$
c_{1s2s}^{3s2p}	$-4.07 \cdot 10^{-3}$	$-4.64 \cdot 10^{-3}$	$-3.86 \cdot 10^{-3}$
c_{1s2s}^{3p2p}	$+4.83 \cdot 10^{-3}$	$+5.42 \cdot 10^{-3}$	$+4.52 \cdot 10^{-3}$
$E^{(4)}$ (a.u.)	—	$-6.43 \cdot 10^{-4}$	$-4.70 \cdot 10^{-4}$
$E^{(5)}$ (a.u.)	—	$+4.6 \cdot 10^{-6}$	$+3.0 \cdot 10^{-6}$
Total energy increment (a.u.)	$-5.00 \cdot 10^{-4}$	$-6.38 \cdot 10^{-4}$	$-4.67 \cdot 10^{-4}$

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Erratum

Homochiralität als Klassifizierungsprinzip von Molekülen spezieller Molekülklassen

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Bei den Formeln auf S. 190 unten sind die Indizes 2 und 3 vertauscht. Die Formeln lauten richtig:

$$\lambda_1, \lambda_3 < \lambda_2, \lambda_4$$

$$\lambda_1 \to \lambda_1' = \lambda_3\,; \quad \lambda_3 \to \lambda_3' = \lambda_1\,; \quad \lambda_2 \to \lambda_2' = \lambda_4\,; \quad \lambda_4 \to \lambda_4' = \lambda_2\,.$$