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On the Contribution of Higher-Order Excitations to Correlation Energies: The Ground State of the Water Molecule

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Using the results of a configuration interaction calculation reported by Rosenberg and Shavitt, we derive an approximation to the correlation energy which may be associated with the sum to infinite order of all linked diagrams involving singly- and doubly-excited states. This result is compared with that obtained by calculation of the energy through third-order. The fourth-order linked diagrams involving quadruply-excited states are computed. It is shown that there is a considerable degree of cancellation between the fourth-order linked diagram energy terms involving doubly-excited intermediate states only and those which contain quadruply-excited states.

Key words: Higher-order excitations, contribution of ~ to correlation energies – Water molecule

1. Introduction

Brueckner [1] first pointed out the importance of ensuring that expressions for the correlation energy of a many-electron system depend linearly on the number of electrons, N, in the system. He demonstrated that certain terms in the Rayleigh–Schrödinger perturbation expansion for the correlation energy depend on N^2, $N^3, \ldots$, but that the series could be rearranged such that these unphysical terms mutually cancel in each order. This result was generalized to all orders by Goldstone [2] giving the well known linked diagram expansion of many-body perturbation theory [3].

It has been demonstrated [4–8] that the many-body perturbation theory, when taken through third-order in the energy, yields results which compare favourably with other methods, such as configuration interaction, for small closed-shell systems. Moreover, a previous treatment [7] of the water molecule has examined the extent

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to which a consistent set of equilibrium structural parameters can be determined from perturbative energy calculations through third-order. As with other finite basis set methods, the perturbative approach has been found to depend critically on the degree of completeness of the basis as measured by its size and quality of composition.

For systems consisting of more than a few (~ 4) electrons the method of configuration interaction is often limited to all singly- and doubly-excited configurations. It is well known that this truncation of the configuration interaction expansion leads to various unphysical terms, having an incorrect dependence on the number of electrons, which would be removed by including more highly-excited configurations. In the perturbative analysis of the configuration interaction energy, this difficulty first arises at fourth-order where unlinked diagrams involving only doubly-excited configurations are cancelled by unlinked diagrams involving quadruply-excited states. These fourth-order unlinked diagrams are shown in Fig. 1. However, we can easily correct limited configuration interaction results for this effect and also for a class of higher-order unlinked diagrams. Thus, we obtain the sum of all linked diagrams involving only limited (usually singles and doubles) excitation to infinite order [9] plus some residual unlinked terms of sixth- and higher-order. For small closed-shell systems, most of the electron correlation energy may be accounted for by considering excitations which are doubly-excited with respect to the reference function. This is explained by the fact that the exclusion principle prevents the close approach of more than two electrons.

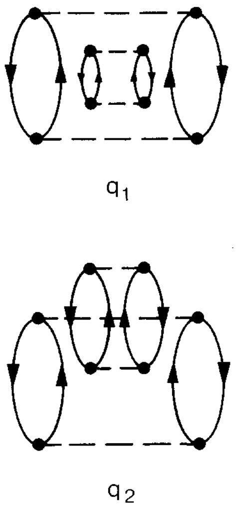

Fig. 1. Fourth-order unlinked diagrams involving quadruply-excited intermediate states

After doubly-excited configurations, the next most important component of the correlation energy for small closed-shell systems is expected to be that associated with configurations which are quadruply-excited with respect to the Hartree–Fock reference function. These terms arise for the first time in the perturbation expansion in second-order in the wavefunction and fourth-order in the energy. All second-order wavefunction terms involving quadruply-excited configurations are of the disconnected cluster type [10–11]. Some fourth-order energy diagrams involving quadruply-excited states are linked; some are unlinked. The unlinked diagrams in the perturbation series cancel, as they must because of their unphysical nature. The linked diagrams are shown in Fig. 2.

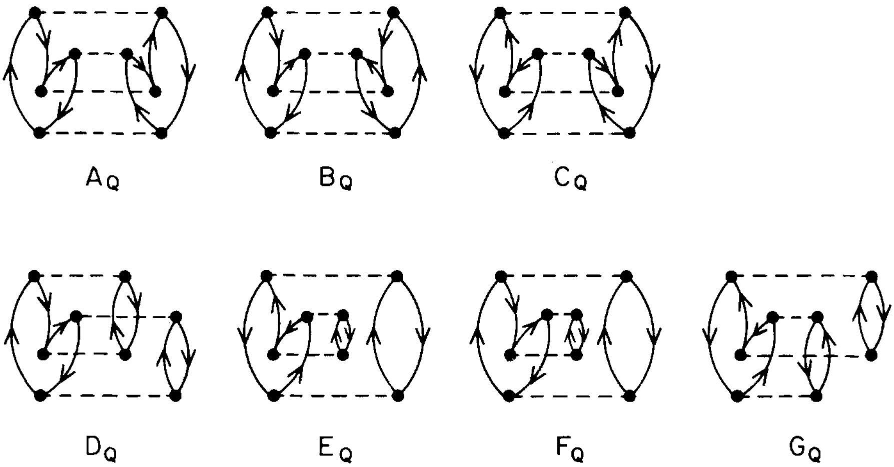

Fig. 2. Fourth-order linked diagrams involving quadruply-excited intermediate states

In this work, we report calculations of the correlation energy of the ground state of the water molecule through third-order in the energy. We use the basis set of 39 Slater exponential functions employed by Rosenberg and Shavitt [12] in their configuration interaction study. From the configuration interaction calculation, which included all singly- and doubly-excited configurations we derive the energy associated with all linked diagrams involving singly- and doubly-excited states to all orders in perturbation theory. The components of the correlation energy corresponding to the fourth-order diagrams involving quadruply-excited states are rigorously evaluated. These energy contributions are compared with higher order terms arising strictly from doubly-excited configurations [13]. (The present results also provide a confirmation of the corrections appearing in the erratum of Bartlett and Shavitt [13].)

Theoretical aspects of the present work are given in the following section. In Sect. 3, we present our results, while in the final section we discuss their significance.

2. Theoretical Aspects

The diagrammatic Rayleigh–Schrödinger perturbation expansion through third-order in the energy forms the basis of a non-iterative and computationally efficient algorithm for electronic structure calculations. Details of the present formulation within the algebraic approximation have been given elsewhere [4, 14].

Following our previous work [4], two different perturbation expansions are investigated corresponding to two choices of the reference Hamiltonian, the "model" and the "shifted" schemes. In the model scheme the Hartree–Fock operator is used as a reference Hamiltonian. In the shifted expansion, the reference Hamiltonian is defined by

$$\sum_{K} |K\rangle \langle K|\mathscr{H}|K\rangle \langle K| \tag{1}$$

where $\mathscr{H}$ is the total Hamiltonian and $|K\rangle$ denotes an N-electron determinant. In addition to the sum of the energy components through third-order, we also construct [2/1] Padé approximants [15] and upper bounds to the energy. Components of the correlation energy will be denoted by $E_a^b(A)$ where a denotes the order of perturbation, b the number of bodies involved (i.e. the number of hole lines) and A, when necessary, denotes the particular diagram.

For the model perturbation expansion we evaluate the fourth-order energy diagrams involving quadruply-excited states. The energy expressions corresponding to such diagrams may be put in the form [16]

$$\sum_{\mu} f_\mu g_\mu \tag{2}$$

where f_μ and g_μ are "second-order" quantities which differ only in their denominators. μ denotes a compound index. It should be noted that some of the terms in this expansion violate the exclusion principle, but these are cancelled by similar terms which correspond to unlinked diagrams.

The configuration interaction calculation of Rosenberg and Shavitt [12] may be corrected for certain unphysical unlinked diagrams. The correction to be used here is [1, 9, 17].

$$\frac{1 - C_0^2}{C_0^2} E_{SD} \tag{3}$$

where C_0 is the coefficient of the root configuration in the configuration interaction expansion and E_{SD} the correlation energy corresponding to such a calculation involving all singly- and doubly-excited functions. The total correlation energy for linked diagrams associated with singly- and doubly-excited states is therefore

$$\frac{1}{C_0^2} E_{SD}.$$

The basis set employed in this work is that of Rosenberg and Shavitt which is based on that of Dunning *et al.* [18]. Integrals over the 39 Slater basis functions are evaluated by the programs of Stevens [19] as adapted for the ATMOL3 programs by Saunders [20].

3. Results

The results of the perturbative calculations through third-order in the energy are given in Table 1. The individual diagrammatic third-order contributions are in general larger in magnitude for the model scheme than the corresponding energy

Table 1. Components of the correlation energy for the water molecule through third-order[a]

	Reference operator	
Energy quantity	$\hat{\mathscr{H}}$ model	$\hat{\mathscr{H}}$ shifted
E_2	-0.28178	-0.34361
$E_3(pp)$	$+0.04990$	$+0.03699$
$E_3^2(hp)$	-0.14003	-0.03846
$E_3^3(hp)$	$+0.04244$	$+0.07158$
$E_3(hp)$	-0.09759	$+0.03312$
$E_3^2(hh)$	$+0.04094$	0.0
$E_3^3(hh)$	$+0.00014$	$+0.00016$
$E_3^4(hh)$	$+0.00336$	$+0.00517$
$E_3(hh)$	$+0.04444$	$+0.00533$
E_3	-0.00325	$+0.07545$
$E_2 + E_3$	-0.28503	-0.26816
$E[2/1]$	-0.28507	-0.28174
γ opt	$+0.95555$	$+0.77048$
E opt	-0.26926	-0.26475

[a] In Hartree.

contribution in the shifted expansion. Nevertheless, the total third-order energy in the model scheme is an order of magnitude smaller than E_3 in the shifted scheme. The formation of the [2/1] Padé approximant brings the two third-order results within 0.0033 Hartrees. As in previously reported calculations [4–8] the formation of the Padé approximant leads to little change in the model energy. The programs used to perform these calculations has been described elsewhere [14]. The present calculations through third-order used 450 kilobytes of storage and 5m 6s of CPU time on the IBM 370/165 computer at the Daresbury Laboratory.

The pair energies obtained in the present study are compared with those of Rosenberg and Shavitt [12] (configuration interaction) and with those of Meyer [21] (independent pair approximation) in Table 2. The present perturbation pair energies are in general much closer in agreement with the configuration interaction pair energies than with the independent pair approximation. This is particularly true of the model expansion. Of course it should be remembered that the calculations of Meyer [21] employed a different basis set than the remaining results in Table 2.

The fourth-order energy terms arising from quadruply-excited states in the model scheme are given in Table 3. The total linked and unlinked energy contribution corresponding to all diagrams in Figs. 1 and 2 is negative definite. However, the unlinked terms cancel against another term in the perturbative expansion: $-E_2S_{11}$, where S_{11} is the self-overlap or normalization integral over the first-order wavefunction. Thus, the residual total contribution consists of the linked diagram total. The individual diagrammatic components of the linked energy are both positive and negative and thereby partially cancel giving a small positive total. The evalua-

Table 2. Electron pair energies for the water molecule from configuration interaction, independent pair approximation, many-body perturbation calculations[a]. I: From the configuration interaction calculation of Rosenberg and Shavitt [12], II: From the independent pair approximation calculation of Meyer [21], III: Present work: "Model" perturbation expansion through third-order, IV: Present work: "Shifted" perturbation expansion through third-order

	I	II	III	IV
$1a_1^2$	0.0315	0.0390	0.0314	0.0315
$1a_1 2a_1$	0.0036	0.0039	0.0036	0.0037
$2a_1^2$	0.0114	0.0122	0.0111	0.0113
$1a_1 1b_2$	0.0025	0.0035	0.0025	0.0025
$2a_1 1b_2$	0.0244	0.0275	0.0251	0.0260
$1b_2^2$	0.0256	0.0264	0.0246	0.0254
$1a_1 3a_1$	0.0033	0.0045	0.0033	0.0034
$2a_1 3a_1$	0.0217	0.0248	0.0221	0.0230
$1b_2 3a_1$	0.0428	0.0434	0.0444	0.0471
$3a_1^2$	0.0251	0.0267	0.0240	0.0250
$1a_1 1b_1$	0.0035	0.0051	0.0036	0.0036
$2a_1 1b_1$	0.0227	0.0268	0.0232	0.0242
$1b_2 1b_1$	0.0405	0.0415	0.0423	0.0450
$3a_1 1b_1$	0.0434	0.0452	0.0454	0.0483
$1b_1^2$	0.0252	0.0267	0.0243	0.0252
"Sum of pairs" energy	0.327362	0.358019	0.330965	0.345071

[a] In Hartree.

Table 3. Components of the correlation energy of the water molecule corresponding to fourth-order diagrams involving quadruply-excited states

	Energy[a]
Linked diagrams	
$E_4(A_Q)$	-0.00714
$E_4(B_Q + C_Q)$	-0.00102
$E_4(D_Q + E_Q)$	$+0.00351$
$E_4(F_Q + G_Q)$	$+0.00786$
Total (linked)	$+0.00321$
Unlinked diagrams	
$E_2 S_{11}$	-0.01711
Total (linked and unlinked)	-0.01391

[a] In Hartree: these energy quantities correspond to the "model" perturbation expansion.

tion of the linked fourth-order terms required 232 kilobytes of storage and 2m 33s of CPU time on the IBM 370/165 computer.

In Table 4, the various energy quantities which may be derived from the results of Rosenberg and Shavitt [12] are given, corresponding to Eqs. (3) and (4). The last line in Table 4 represents an *ad hoc* addition of the extrapolated linked diagram energy associated with singly- and doubly-excited states plus the fourth-order linked diagram contribution arising from quadruply excited states.

Table 4. Energy quantities for the water molecule derived from the configuration interaction calculation of Rosenberg and Shavitt [12]

	Energy[a]
E_{SD}	−0.27558
C_0	+0.97242
$\frac{1 - C_0^2}{C_0^2} E_{SD}$	−0.01585
$\frac{1}{C_0^2} E_{SD}$	−0.29143
$\frac{1}{C_0^2} E_{SD} + E_4(A_Q + \cdots + G_Q)$	−0.28822

[a] In Hartree.

4. Discussion

The model perturbation expansion based on the use of the Hartree–Fock operator as a reference Hamiltonian appears to be more rapidly convergent on the basis of a criterion of E_3/E_2 than the shifted perturbation expansion in the present study. This conclusion is consistent with the earlier results on water [7] and therefore the total energies compiled in Table 5 contain the model results and the various configuration interaction results for comparison. The infinite order sum of all linked diagrams, E_{SD} (linked), involving singly- and doubly-excited configurations is lower than the third-order energy obtained from the model perturbation expansion by −0.0064 Hartrees, or 2.2% of the third-order result. On the other hand, the third-order result arising from the shifted perturbation expansion differs from the infinite order result by −0.0201 Hartree, or 7.5%. The formation of Padé approximants brings the results obtained from the two perturbation series to within 1.2% of each other.

The linked diagrams involving quadruply-excited states that arise in fourth-order are found to contribute +0.0032 Hartree in the case of the water molecule. However, the fourth-order linked diagram contribution arising from doubly-excited

Table 5. Non-relativistic energies for the water molecule[a]

	Total energy	Correlation energy
E_{ref}	−76.064226	
$E_{\text{ref}} + E_2 + E_3$	−76.3493	−0.2850
Padé approximant	−76.3493	−0.2850
Perturbative upper bound	−76.3335	−0.2693
E_{SD}	−76.3398	−0.2756
E_{SD} (linked)	−76.3557	−0.2914
E_{SD} (linked) + E_{4Q} (linked)	−76.3524	−0.2882
Non-relativistic, clamped nuclei energy	−76.4376 ± 0.0024	−0.370 ± 0.003

[a] In Hartree.

states has been found [13] to be −0.00432 Hartree. Thus again a cancellation of diagrammatic energy contributions within a given order of the perturbation expansion is apparent. The net calculated fourth-order energy from doubly- and quadruply-excited states is −0.0011 Hartree. Clearly, the inclusion of diagrams involving doubly-excited configurations beyond third-order is not justified unless the quadruply-excited functions are also included, and vice versa. Since singly- and triply-excited states also enter the perturbation expansion at fourth-order, it would be equally inconsistent to omit either of these contributions in a fourth-order calculation of the energy.

A natural question to pose is to what order of the perturbation expansion should a calculation be performed. A third-order calculation is quite efficient and economical [14], and using the model perturbation scheme, the third-order results appear to be within a few per cent of the infinite order results and give good indication of convergence [7]. A full fourth-order calculation is far more difficult and at best might recover several millihartree of energy. From Table 5, the limitation imposed by the size and quality of the given 39 orbital basis set is about −0.09 Hartree. Thus it might be more reasonable to improve the basis set and retain the third-order level of perturbation theory rather than pursue the small additional residue coming from fourth- and higher-order terms.

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Note added in proof

The contribution of triply-excited states to the correlation energy of the water molecule has recently been examined [22] and the full fourth-order energy discussed.