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Commentationes

A Note on the Relation between CI and Rayleigh-Schrödinger Perturbation Theory

M. KLEINER
Department of Chemistry, The University, Sheffield S3 7HF, England

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Energy expressions to the 4th order of accuracy are derived from a partitioned CI matrix; these expressions are identical in each order, to the corresponding formulas derived in the frame of Rayleigh-Schrödinger perturbation theory.

Von einer aufgespaltenen CI-Matrix werden Energieausdrücke bis zur 4. Ordnung entwickelt. Diese Ausdrücke sind für jede Ordnung identisch mit den im Rahmen der Rayleigh-Schrödingerschen Störungstheorie entwickelten Formeln.

1. Introduction

One of the main deficiencies in the Hartree-Fock method is that a single determinant represents a wave function, which in principle must be approximated by an infinitely long expansion. To correct this inadequacy more terms are needed, which are conventionally introduced by means of admitting configuration interaction (CI). Numerous studies have confirmed the favourable effect that either full or judicious inclusion of CI has on the wave function and on the expectation values derived from it. Recent detailed studies have been made on Benzene [1] and on CO [2]. Although CI admission is in principle a straightforward process, in practice the labour involved may quickly become prohibitively expensive. Suppose $2N$ electrons and K atomic orbitals are involved ($K \geqq N$), then for full CI (limiting ourselves to singlet states only) in a basis that extends over all possible eigenfunctions of the S^2 operator, one has to build and diagonalize a matrix of size

$$M = \sum_{L=0}^{t} \binom{K-2L}{N-L} \binom{K}{2L} \frac{(2L)!}{L!\,(L+1)!} \qquad \begin{array}{ll} t = K-N, & K < 2N \\ t = N, & K \geqq 2N \end{array} \tag{1}$$

corresponding to all possible $0, 1, 2, 3, \ldots, 2N$ excitations[1]. Even for a relatively small system comprized of 4 electrons and 6 orbitals (say, LiH in a double zeta basis), Eq. (1) yields $M = 105$, which is already quite large. It is concluded that

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[1] General expressions for M, the dimension of a CI problem over a basis of S^2 operator eigenfunctions, as a function of K, N and S ($2S+1$ being the state multiplicity) have been previously given by Mulder [17], and by other authors listed in his paper. The derivation of Eq. (1) in the present communication is similar in approach to that given by [17], but differs from it in some details. It is therefore documented in the Appendix.

except for very small systems, the effort needed to overcome the CI size barrier may outweigh that invested in computing the basic molecular integrals. Clearly a simplifying procedure is needed; in looking for a device to reduce the CI scheme to manageable dimensions one may resort to Perturbation Theory [3–6]. According to standard Rayleigh-Schrödinger perturbation theory (henceforth RS) and with the familiar notation ($\boldsymbol{H} = \boldsymbol{H}^0 + \varepsilon \boldsymbol{H}'$; $\varepsilon \to 1$), one has for the correct energy of a perturbed level n:

$$E_n = E_n^0 + \varepsilon E_n' + \varepsilon^2 E_n'' + \cdots = E_n^0 + \langle \psi_n^0 | \boldsymbol{H}' | \psi_n^0 \rangle + \sum_{m \neq n} \frac{\langle \psi_n^0 | \boldsymbol{H}' | \psi_m^0 \rangle^2}{E_n^0 - E_m^0} + \cdots \tag{2}$$

where the power of ε determines the order of the perturbation. To make the connection with CI one formally equates integrals of type H'_{nm} in (2) with the nm'th CI matrix element; thus the molecular Hamiltonian implicitly assumes the role of a perturbation between the energy levels. Recently this procedure was examined in detail [7–11]. The numerical results obtained by these authors suggest that in many cases it would be feasible to apply second (or higher) order perturbation theory to proceed beyond the SCF limit. In view of these encouraging results, it would be useful to elaborate on the formal relation between the CI and RS methods, in the particular context of MO calculations. While the relation is well understood from the RS tail, it is not as clear when one assumes no knowledge of RS. Our starting point therefore will be the CI *matrix*; it will be stepwise and approximately diagonalized. At each stage the expressions for the resulting eigenvalues will be examined and the various matrix elements involved assigned numerical values in a manner that will indicate the relation to RS, subject to the particular partitioning described next.

2. Approximate Diagonalization

The CI matrix is constructed according to Slater's rules [12]. Zero's are put either for matrix elements of two states differing in more than two orbitals, or according to Brillouin's theorem, for $\left\langle \text{G.S.} | H | E \overset{n}{\underset{m}{\uparrow}} \right\rangle$; the symbol $E \overset{n}{\underset{m}{\uparrow}}$ stands for: E = state; m = orbital excited from; n = orbital excited to; ↑ = excitation. Virtual orbitals are used for building the various excited states [13]. For the diagonal elements, closed expressions for states of type $E \overset{c}{\underset{a}{\uparrow}} \overset{d}{\underset{b}{\uparrow}}$ $a \neq b$, $c \neq d$ or lesser complexity have been given [14]. $\boldsymbol{B}$ is now the CI matrix (Fig. 1).

We have now a Hermitian matrix with the property: diagonal elements $\gg$ off-diagonal elements. The matrix $\boldsymbol{B}$ is in the mathematical sense "perturbed" [15] and we may assume that it can be expanded in a converging matrix series; ε is a small parameter which labels "order",

$$\boldsymbol{B} = \boldsymbol{B}^0 + \varepsilon \boldsymbol{B}^{\mathrm{I}} + \varepsilon^2 \boldsymbol{B}^{\mathrm{II}} + \cdots \tag{3}$$

where the $\boldsymbol{B}$'s do not depend on ε. Let $\boldsymbol{S}$ be an as yet undetermined unitary matrix of the form

$$\boldsymbol{S} = \boldsymbol{S}^0 + \varepsilon \boldsymbol{S}^{\mathrm{I}} + \varepsilon^2 \boldsymbol{S}^{\mathrm{II}} + \cdots . \tag{4}$$

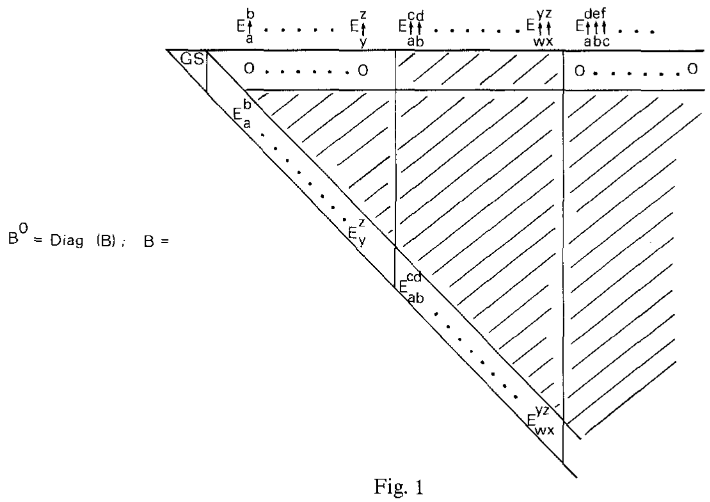

Fig. 1

We adjust S in such a way that

$$A = SBS^{-1} \qquad A = \mathrm{Diag}(\lambda_1 \ldots \lambda_m)\,. \tag{5}$$

S can always be chosen[2] to yield $A_{nn} = \lambda_n$, i.e. the eigenvalues of A and B are identical in magnitude and order along the diagonal. It is suggested from (3), (4) and (5) that A can also be expanded in terms of a converging matrix series

$$A = A^0 + \varepsilon A^{\mathrm{I}} + \varepsilon^2 A^{\mathrm{II}} + \cdots \tag{6}$$

all the A's being diagonal. Our aim now is to compute A. Substitution into a rearranged (5) the series on the right of (3), (4) and (6) yields

$$(A^0 + \varepsilon A^{\mathrm{I}} + \varepsilon^2 A^{\mathrm{II}} + \cdots)(S^0 + \varepsilon S^{\mathrm{I}} + \varepsilon^2 S^{\mathrm{II}} + \cdots) = (S^0 + \varepsilon S^{\mathrm{I}} + \varepsilon^2 S^{\mathrm{II}} + \cdots)(B^0 + \varepsilon B^{\mathrm{I}} + \cdots) \tag{7}$$

if (7) is to hold identically in the successive powers of ε, the following sequence of matrix equations must hold

$$A^0 S^0 = S^0 B^0 \tag{8}$$

$$A^0 S^{\mathrm{I}} + A^{\mathrm{I}} S^0 = S^0 B^{\mathrm{I}} + S^{\mathrm{I}} B^0 \tag{9}$$

$$A^0 S^{\mathrm{II}} + A^{\mathrm{I}} S^{\mathrm{I}} + A^{\mathrm{II}} S^0 = S^0 B^{\mathrm{II}} + S^{\mathrm{I}} B^{\mathrm{I}} + S^{\mathrm{II}} B^0\,. \tag{10}$$

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The only quantities in these equations which are known from the outset are the elements of B, i.e. the elements of the CI matrix. It is possible, however, with the help of Eqs. (8–11) to set up one after the other the A's and the S's to determine A to any degree of accuracy. Now, as we cannot separate the different orders of the B's, we are left with some freedom to assign their values, subject to (3) as constraint. This can be done in a manner that suits the context of a particular

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[2] By elementary row and column operations.

problem. To obtain full agreement with expressions derived from RS [9] one must choose for the $\boldsymbol{B}$'s

$$B^0_{ij} = \begin{cases} \neq 0, & i=j \quad \text{(and not degenerate)} \\ =0, & i \neq j \end{cases}$$
$$B^{\mathrm{I}}_{ij} = \begin{cases} =0, & i=j \\ \neq 0, & i \neq j \end{cases} \tag{12}$$
$$\boldsymbol{B}^{\mathrm{II}} = \boldsymbol{B}^{\mathrm{III}} = \cdots = 0\,.$$

This choice can of course be made independently of the RS method. Previously the flexibility in partitioning the Hamiltonian in the context of CI was noted by [7].

3. Diagonalization to First Order

Let $\varepsilon \to 0$ so that $\boldsymbol{B} \to \boldsymbol{B}^0$ and $\boldsymbol{S} \to \boldsymbol{S}^0$. Then since the eigenvalues of $\boldsymbol{A}$ are the same as those of $\boldsymbol{B}$ (identity also in order along the diagonal, as is in (5) above) $\boldsymbol{A}^0 = \boldsymbol{B}^0$ and (8) becomes

$$\boldsymbol{B}^0 \boldsymbol{S}^0 = \boldsymbol{S}^0 \boldsymbol{B}^0\,. \tag{13}$$

As $\boldsymbol{S}$ must be unitary for any ε it follows that when $\varepsilon \to 0$, $\boldsymbol{S}^0$ is unitary. It can be verified (see Appendix) that a unitary matrix ($\boldsymbol{S}^0$) which commutes with a non-degenerate diagonal matrix ($\boldsymbol{B}^0$ in (13)) must be diagonal itself and each of its diagonal elements be of modulus unity. We choose

$$\boldsymbol{S}^0 = \boldsymbol{1}\,. \tag{14}$$

Now it follows from (13) and (14) that (9) takes the form

$$\boldsymbol{B}^0 \boldsymbol{S}^{\mathrm{I}} - \boldsymbol{S}^{\mathrm{I}} \boldsymbol{B}^0 = \boldsymbol{B}^{\mathrm{I}} - \boldsymbol{A}^{\mathrm{I}}\,. \tag{15}$$

The nn'th element on both sides of (15) can be written

$$\sum_i B^0_{ni} S^{\mathrm{I}}_{in} - \sum_i S^{\mathrm{I}}_{ni} B^0_{in} = B^{\mathrm{I}}_{nn} - A^{\mathrm{I}}_{nn} = 0 \tag{16}$$

since $\boldsymbol{B}^0$ is diagonal. Hence

$$A^{\mathrm{I}}_{nn} = B^{\mathrm{I}}_{nn}\,. \tag{17}$$

If powers of ε higher than the first are neglected, (6) reduces to $\boldsymbol{A} = \boldsymbol{A}^0 + \varepsilon \boldsymbol{A}^{\mathrm{I}}$, or, in view of Eqs. (2) and (17)

$$\lambda_n = B^0_{nn} + \varepsilon B^{\mathrm{I}}_{nn}\,. \tag{18}$$

Eq. (18) is identical to the expression corrected to first order in the RS method. According to the convention adopted for the $\boldsymbol{B}$'s in Eqs. (12), $B^{\mathrm{I}}_{nn} = 0$ and (18) reduces to

$$\lambda_n = B^0_{nn} \tag{19}$$

– a similar expression was derived on different grounds in [3]. It should be noted that here, $B^{\mathrm{I}}_{nn}=0$ was adopted as a basic assumption due to our particular partitioning of the CI matrix and does not follow from the quality of the zero order wave function.

4. Diagonalization to Second Order

It can be verified from (9), (13) and (16) (see Appendix) that[3]

$$S^{\mathrm{I}}_{ij}=\begin{cases}0, & i=j\\ \dfrac{B^{\mathrm{I}}_{ij}}{B^0_{ii}-B^0_{jj}}, & i\neq j\,.\end{cases} \tag{20}$$

From a rearranged (10) and taking advantage of (14) one finds

$$\boldsymbol{A}^{\mathrm{II}}=\boldsymbol{B}^{\mathrm{II}}+\boldsymbol{S}^{\mathrm{I}}\boldsymbol{B}^{\mathrm{I}}-\boldsymbol{A}^{\mathrm{I}}\boldsymbol{S}^{\mathrm{I}}+\boldsymbol{S}^{\mathrm{II}}\boldsymbol{B}^0-\boldsymbol{B}^0\boldsymbol{S}^{\mathrm{II}} \tag{21}$$

for the diagonal elements of $\boldsymbol{A}^{\mathrm{II}}$ one need consider only (22) (as $\boldsymbol{A}^{\mathrm{I}}\boldsymbol{S}^{\mathrm{I}}$ vanishes along the diagonal and $\boldsymbol{B}^0$ is diagonal)

$$(\boldsymbol{A}^{\mathrm{II}})_{nn}=B^{\mathrm{II}}_{nn}+(\boldsymbol{S}^{\mathrm{I}}\boldsymbol{B}^{\mathrm{I}})_{nn}=B^{\mathrm{II}}_{nn}+\sum_{i\neq n}\frac{B^{\mathrm{I}}_{ni}B^{\mathrm{I}}_{in}}{B^0_{nn}-B^0_{ii}} \tag{22}$$

thus, to the second power of ε the diagonal elements of $\boldsymbol{A}$ take now the full form

$$\lambda_n=B^0_{nn}+\varepsilon B^{\mathrm{I}}_{nn}+\varepsilon^2\left[B^{\mathrm{II}}_{nn}+\sum_{i\neq n}\frac{B^{\mathrm{I}}_{ni}B^{\mathrm{I}}_{in}}{B^0_{nn}-B^0_{ii}}\right] \tag{23}$$

when the convention in (12) is introduced (23) is reduced to (24) – an expression derived from RS by Moller-Plesset [3], and used by Nesbet [4] for the approximate diagonalization of large matrices.

$$\lambda_n=B^0_{nn}+\sum_{i\neq n}\frac{B^{\mathrm{I}}_{ni}B^{\mathrm{I}}_{in}}{B^0_{nn}-B^0_{ii}}\,. \tag{24}$$

5. Diagonalization to Third and Fourth Order

From (10), (13) and (14) one obtains

$$\boldsymbol{A}^0\boldsymbol{S}^{\mathrm{II}}-\boldsymbol{S}^{\mathrm{II}}\boldsymbol{B}^0=\boldsymbol{B}^{\mathrm{II}}-\boldsymbol{A}^{\mathrm{II}}+\boldsymbol{S}^{\mathrm{I}}\boldsymbol{B}^{\mathrm{I}}-\boldsymbol{A}^{\mathrm{I}}\boldsymbol{S}^{\mathrm{I}} \tag{25}$$

which leads, noting that the $\boldsymbol{A}$'s are diagonal, to

$$S^{\mathrm{II}}_{ij}=\begin{cases}0, & i=j\\ \dfrac{B^{\mathrm{II}}_{ij}}{B^0_{ii}-B^0_{jj}}+\dfrac{1}{B^0_{ii}-B^0_{jj}}\left(\displaystyle\sum_{l\neq i}\frac{B^{\mathrm{I}}_{il}B^{\mathrm{I}}_{lj}}{B^0_{ii}-B^0_{ll}}-\frac{B^{\mathrm{I}}_{ii}B^{\mathrm{I}}_{ij}}{B^0_{ii}-B^0_{jj}}\right), & i\neq j\end{cases} \tag{26}$$

substituting to (10) and, as only diagonal elements of $\boldsymbol{A}^{\mathrm{III}}$ are needed (this eliminates terms originating from $\boldsymbol{A}^{\mathrm{I}}\boldsymbol{S}^{\mathrm{II}}$, $\boldsymbol{A}^{\mathrm{II}}\boldsymbol{S}^{\mathrm{I}}$ and causes disappearance of $\boldsymbol{S}^{\mathrm{II}}\boldsymbol{B}^0-\boldsymbol{B}^0\boldsymbol{S}^{\mathrm{II}}$) we

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[3] As we are not interested in "Expectation Values" here, the columns of $\boldsymbol{S}$ matrices will not be renormalized at successive intermediate steps.

have

$$\begin{aligned} A^{\mathrm{III}}_{nn} &= B^{\mathrm{III}}_{nn} + \sum_j S^{\mathrm{I}}_{nj} B^{\mathrm{II}}_{jn} + \sum_j S^{\mathrm{II}}_{nj} B^{\mathrm{I}}_{jn} = B^{\mathrm{III}}_{nn} + 2 \sum_{j\neq n} \frac{B^{\mathrm{I}}_{nj} B^{\mathrm{II}}_{jn}}{B^0_{nn} - B^0_{jj}} \\ &+ \sum_{j\neq n} \sum_{l\neq n} \frac{B^{\mathrm{I}}_{nl} B^{\mathrm{I}}_{lj} B^{\mathrm{I}}_{jn}}{(B^0_{nn} - B^0_{ll})(B^0_{nn} - B^0_{jj})} - \sum_{j\neq n} \frac{B^{\mathrm{I}}_{nn} B^{\mathrm{I}}_{nj} B^{\mathrm{I}}_{jn}}{(B^0_{nn} - B^0_{jj})^2} \end{aligned} \tag{27}$$

on introduction of the conditions specified in (12) the first two terms on the right hand of (27) disappear, and one remains with the third order expression in the RS theory. However, because of B^{I}_{nn}, the last term also disappears and only one term is left. Thus we have the third order correction for λ_n

$$A^{\mathrm{III}}_{nn} = \sum_{j\neq n} \sum_{l\neq n} \frac{B^{\mathrm{I}}_{nl} B^{\mathrm{I}}_{lj} B^{\mathrm{I}}_{jn}}{(B^0_{nn} - B^0_{ll})(B^0_{nn} - B^0_{jj})} \tag{28}$$

a simplification that viewed from RS [3, 7, 8] results from the particular nature of the variationally obtained SCF energy. A similar treatment yields for S^{III}_{ij} and for A^{IV}_{nn}, the correction to 4th order

$$S^{\mathrm{III}}_{ij} = \begin{cases} 0, & i=j \\ \dfrac{1}{B^0_{ii} - B^0_{jj}} \left(\displaystyle\sum_{k\neq i} \sum_{l\neq i} \frac{B^{\mathrm{I}}_{il} B^{\mathrm{I}}_{lk} B^{\mathrm{I}}_{kj}}{(B^0_{ii} - B^0_{ll})(B^0_{ii} - B^0_{kk})} - \sum_{l\neq i} \frac{B^{\mathrm{I}}_{il} B^{\mathrm{I}}_{li} B^{\mathrm{I}}_{ij}}{(B^0_{ii} - B^0_{ll})(B^0_{ii} - B^0_{jj})} \right), & i\neq j \end{cases} \tag{29}$$

$$\begin{aligned} A^{\mathrm{IV}}_{nn} &= \sum_{i\neq n} \sum_{j\neq n} \sum_{l\neq n} \frac{B^{\mathrm{I}}_{ni} B^{\mathrm{I}}_{ij} B^{\mathrm{I}}_{jl} B^{\mathrm{I}}_{ln}}{(B^0_{nn} - B^0_{ii})(B^0_{nn} - B^0_{jj})(B^0_{nn} - B^0_{ll})} \\ &- \sum_{i\neq n} \sum_{j\neq n} \frac{B^{\mathrm{I}}_{ni} B^{\mathrm{I}}_{in} B^{\mathrm{I}}_{nj} B^{\mathrm{I}}_{jn}}{(B^0_{nn} - B^0_{ii})(B^0_{nn} - B^0_{jj})^2}. \end{aligned} \tag{30}$$

6. Discussion

A scheme was described in which the CI matrix served as a starting point for the derivation of energy expressions identical to those obtained in the RS frame. A particular partitioning of the CI matrix allowed for the simplifications similar to those due to Moller-Plesset [3].

It must be emphasized, following [16], that this identity is formal, as it depends on the partitioning of the CI matrix. It appears that the CI method is related to the "Variation Perturbation" method [16], which encompasses RS as a special case. We now consider briefly the reasoning which leads to the partitioning adopted in (12). For concreteness the expression in (27) is examined. It was initially derived for a Hamiltonian of the general form $\boldsymbol{B} = \boldsymbol{B}^0 + \varepsilon \boldsymbol{B}' + \varepsilon^2 \boldsymbol{B}'' + \cdots$. To make the CI method compatible with ordinary RS, where only 1st order perturbation is usually admitted, we must put $\boldsymbol{B}^{\mathrm{II}} = \boldsymbol{B}^{\mathrm{III}} = \cdots = 0$ and retain only $\boldsymbol{B} = \boldsymbol{B}^0 + \varepsilon \boldsymbol{B}'$. The role of the perturbing matrix $\boldsymbol{B}'$, is to help us assess the effect of extending the basis by adding configurations. At this stage only the last two terms on the left of (27) remain, forming the usual 3rd order correction in RS. A further simplification is obtained from (18). Although (18) in itself is a simple result in RS, it has important implications in the CI context, as it assures that the eigenvalues of $\boldsymbol{B}$ corrected to first order are "diagonal". It follows that provided $\boldsymbol{B}^0$ is taken to be the diagonal part of the original CI matrix, one may put $B^{\mathrm{I}}_{nn}=0$. This choice allows us to simulate the Moller-Plesset [3] results, and to drop the 4th term in (27) leading to the single term expression in (28).

The arguments given above formally justify regarding a CI study for some state n equivalent to an ordinary RS treatment with the following characteristics: $\boldsymbol{H}=\boldsymbol{H}^0+\varepsilon\boldsymbol{H}'$; $\langle\psi^0_n|\boldsymbol{H}'|\psi^0_n\rangle=0$. Eqs. (28) and (30) must therefore be derivable by any of the methods available for construction of correction expressions in RS. One may choose to operate within the scheme of rules formulated by Huby[4] [18]. To apply his "derivation by inspection" method, and using his notation, we define a projection operator

$$\boldsymbol{Q}_0=\sum_{i\neq n}|\psi^0_i\rangle\langle\psi^0_i|,\qquad (\boldsymbol{Q}_0^2=\boldsymbol{Q}_0) \tag{31}$$

(i.e. $\boldsymbol{Q}_0$ is the projector onto the space orthogonal to the state n which is presently under investigation) and an inverse operator $\boldsymbol{a}$

$$\boldsymbol{a}=(E^0_n-\boldsymbol{H}^0)^{-1},\qquad \left((E^0_n-\boldsymbol{H}^0)^{-1}\psi^0_i=\frac{1}{E^0_n-E^0_i}\psi^0_i\right) \tag{32}$$

now it is well known [19] that if

$$E'_n=E''_n=\cdots=E^{(N-1)'}_n=0 \tag{33}$$

then the N'th order correction is given by

$$E^{N'}_n=\left\langle\psi^0_n\middle|\boldsymbol{H}'\left(\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\boldsymbol{H}'\right)^{N-1}\middle|\psi^0_n\right\rangle \tag{34}$$

where (33) reads

$$\langle\psi^0_n|\boldsymbol{H}'|\psi^0_n\rangle=\left\langle\psi^0_n\middle|\boldsymbol{H}'\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\boldsymbol{H}'\middle|\psi^0_n\right\rangle=\cdots=\left\langle\psi^0_n\middle|\boldsymbol{H}'\left(\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\boldsymbol{H}'\right)^{N-2}\middle|\psi^0_n\right\rangle=0.$$

If however only corrections up to the k'th order vanish, $K<N-1$, then additional terms (with the correct sign) must be added to expression (34), which arise from all possible "Bra-ket"-ing internal $\boldsymbol{H}'$ factors in (34), according to the prescription in [18]. For E'''_n we thus have

$$E'''_n=\left\langle\psi^0_n\middle|\boldsymbol{H}'\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\boldsymbol{H}'\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\boldsymbol{H}'\middle|\psi^0_n\right\rangle+(-1)\left\langle\psi^0_n\middle|\boldsymbol{H}'\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\langle\boldsymbol{H}'\rangle\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\boldsymbol{H}'\middle|\psi^0_n\right\rangle \tag{35}$$

however

$$\left\langle\psi^0_n\middle|\boldsymbol{H}'\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\langle\boldsymbol{H}'\rangle\frac{\boldsymbol{Q}_0}{\boldsymbol{a}}\boldsymbol{H}'\middle|\psi^0_n\right\rangle=\left\langle\psi^0_n\middle|\boldsymbol{H}'\frac{\boldsymbol{Q}_0}{\boldsymbol{a}^2}\boldsymbol{H}'\middle|\psi^0_n\right\rangle\langle\psi^0_n|\boldsymbol{H}'|\psi^0_n\rangle=0$$

$(H'_{nn}=0$ by assumption)

and only the first term in (35) survives, which is identical to (28). This identity is easily seen after substituting for $\boldsymbol{Q}_0$ and $\boldsymbol{a}$ their values defined in (31) and (32).

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[4] The author is indebted to a referee for bringing to his attention the papers by Mulder [17] and Huby [18].

Similarly for $E_n^{4'}$ one obtains

$$\begin{aligned} E_n^{4'} = & \left\langle \psi_n^0 \middle| \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \middle| \psi_n^0 \right\rangle \\ & - \left\langle \psi_n^0 \middle| \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \langle \boldsymbol{H}' \rangle \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \middle| \psi_n^0 \right\rangle \\ & - \left\langle \psi_n^0 \middle| \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \langle \boldsymbol{H}' \rangle \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \middle| \psi_n^0 \right\rangle \\ & - \left\langle \psi_n^0 \middle| \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \left\langle \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \right\rangle \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \middle| \psi_n^0 \right\rangle \\ = & \left\langle \psi_n^0 \middle| \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \middle| \psi_n^0 \right\rangle \\ & - \left\langle \psi_n^0 \middle| \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}^2} \boldsymbol{H}' \middle| \psi_n^0 \right\rangle \left\langle \psi_n^0 \middle| \boldsymbol{H}' \frac{\boldsymbol{Q}_0}{\boldsymbol{a}} \boldsymbol{H}' \middle| \psi_n^0 \right\rangle . \end{aligned} \tag{36}$$

Expression (36) is identical to (30) obtained for the fourth order correction by the approximate diagonalization method. The assertion that perturbation corrections may be derived from a CI matrix independently of the RS method is therefore shown to be correct.

Appendix

1. To derive the expression on the right side of (1). Consider $2N$ electrons and K atomic orbitals, and look at a case where L pairs out of the N available are distributed in $2L$ orbitals, each orbital is occupied by a single electron. This can be effected in $\binom{K}{2L}$ ways. Meanwhile the rest of the $N-L$ pairs can be distributed in $\binom{K-2L}{N-L}$ ways between the vacant orbitals. The total number of ways to achieve a situation of $(N-L)$ orbitals doubly occupied and $2L$ orbitals singly occupied is $\binom{K-2L}{N-L}\binom{K}{2L}$. To each of these situations correspond several linearly independent S^2 eigenfunctions, whose total number has been given by [20]. For $2L$ electrons outside a closed shell and a singlet state this number is $\binom{2L}{L} - \binom{2L}{L-1} = \frac{(2L)!}{L!(L+1)!}$. Multiplying this number by the number of realized situation and summing over all L yields

$$M = \sum_{L=0}^{t} \binom{K-2L}{N-L}\binom{K}{2L} \frac{(2L)!}{L!(L+1)!} \qquad \begin{array}{ll} t = K-N, & K < 2N , \\ t = N, & K \geqq 2N . \end{array}$$

Judging by several numerical checks this expression is identical to that given by Mulder's [17] closed formula,

$$M = \frac{K+1}{(N+1)(K-N+1)} \binom{K}{N}^2 .$$

2\. To show that S^0 is diagonal and each S_{ii}^0 is of modulus unity. Starting with $\boldsymbol{S}^0\boldsymbol{B}^0=\boldsymbol{B}^0\boldsymbol{S}^0$, one obtains on performing multiplication: $S_{ij}^0(B_{ii}^0-B_{jj}^0)=0$. As $\boldsymbol{B}^0$ is not degenerate, $S_{ij}^0=0$. Also $\boldsymbol{S}^0$ being unitary leads to $S_{ii}^{0*}\cdot S_{ii}^0=1$, hence $S_{ii}^0=1\cdot\exp(\pm i\theta)$; choose $\theta=0$.

3\. To find S_{ij}^{I}. Since B^0 is diagonal it follows from (16) that S_{ij}^{I} satisfies

$$B_{ii}^0 S_{ij}^{\mathrm{I}}-S_{ij}^{\mathrm{I}}B_{jj}^0=B_{ij}^{\mathrm{I}}\,;\qquad S_{ij}^{\mathrm{I}}=\frac{B_{ij}^{\mathrm{I}}}{B_{ii}^0-B_{jj}^0}\,.$$

Similarly, for S_{ii}^{I}: $B_{ii}^0 S_{ii}^{\mathrm{I}}-S_{ii}^{\mathrm{I}}B_{ii}^0=0$ and S_{ii}^{I} is arbitrary. Choose $S_{ii}^{\mathrm{I}}=0$ to satisfy orthogonality constraints: $\langle \boldsymbol{S}_i^0|\boldsymbol{S}_i^{\mathrm{I}}\rangle=0$. This choice will persist for $S_{ii}^{\mathrm{II}}, S_{ii}^{\mathrm{III}},\ldots$.

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Dr. M. Kleiner
Department of Chemistry
The University
Sheffield S 3 7 HF, England