Theoret. Chim. Acta (Berl.) 40, 157–174 (1975)

Coupled Multiconfiguration Self-Consistent Field (MC SCF) Perturbation Theory*

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Received April 22, 1975

The analytical form of the perturbation theory for the MC SCF method of Veillard and Clementi is presented. The appropriate second-order energy functional which takes into account the self-consistency requirements, leads to a set of coupled first-order perturbed equations determining the perturbed configuration coefficients and orbitals. The second-order energy formula derived from this functional can be given a clear physical interpretation. The present analytical approach is compared with the finite perturbation MC SCF scheme.

The possibility of the approximate solution of the coupled MC SCF perturbation equations is also discussed and the so-called uncoupled procedures are devised. In the limit of the single determinant wave function the present formulae are shown to be equivalent to the appropriate Hartree-Fock perturbation results.

The differences between the one-configuration SCF and the MC SCF approach are illustrated by the calculation of the electric dipole polarizability of H_2 in the CNDO/2 approximation. It is shown that the one-configuration SCF approaches cannot account for the correct asymptotic properties of the second-order energy for large internuclear distances. This feature of the SCF perturbation theories does not depend on the specific approximations of the CNDO/2 scheme and is corrected by using the MC SCF perturbation theory.

Key word: MC SCF perturbation theory

1. Introduction

Until very recently most of the calculations of the second- and higher-order atomic and molecular properties were carried out within the one-electron approximation. A variety of more or less sophisticated one-electron perturbation schemes, based on the zeroth-order self-consistent field (SCF) Hartree-Fock (HF) wave functions, has been devised [1–15]. The main attention has been given to the exact HF approach to the perturbation problem, resulting in the so-called coupled Hartree-Fock (CHF) perturbation theory [1–4, 8, 9, 14]. But even in this case the results, though sometimes quite encouraging [9, 14, 16–18], refer to the correlationless level. Since there is no definite relation between the exact (including correlation) and the CHF perturbed energies, the role of the corresponding correlation corrections cannot be easily predicted [19, 20]. A few calculations using explicitly correlated wave functions [21–24] do not provide any unambiguous

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* Sponsored by the Institute of Low Temperatures and Structure Research, Polish Academy of Sciences, and by the Institute of Mathematics, Polish Academy of Sciences.

answer to this question and their systematic extension for many-electron systems does not seem to be feasible. The use of the Brueckner-Goldstone many-body perturbation theory [25–28] in the molecular perturbation calculations requires an enormous extension of the basis set [28, 29] and suffers from quite obvious limitations. Although this approach provides a systematic tool for the study of the correlation effects, the summation of diagrams usually involves some approximate techniques [27–29]. Moreover, some of recent finite basis set Brueckner–Goldstone [28, 29] calculations of the correlation corrections are in fact equivalent to a very limited and incomplete configuration interaction approach.

The multi-configuration self-consistent field (MC SCF) method can be considered as a natural extension of the traditional HF scheme [30–39]. It recovers quite a good portion of the correlation energy with a relatively small number of included configurations [40]. Some recent applications of the MC SCF method to the calculation of the atomic dipole polarizabilities have shown its unquestionable usefulness [41–43]. These MC SCF calculations were performed according to the so-called finite field perturbation technique and in principle should be equivalent to the self-consistent solution of the first-order perturbed MC SCF equations, i.e., to the coupled MC SCF theory. However, any finite field included in the Hamiltonian will usually change the symmetry of the unperturbed problem and this may affect the asymptotic properties of the computed energies [41]. Also the finite field perturbation techniques require a very high numerical accuracy of the calculations [24], much higher than that for the corresponding unperturbed problem. The resolution of the perturbed equations according to the orders of an appropriate perturbation parameter allows to avoid at least some of the mentioned difficulties of the finite field approach.

It is the aim of the present paper to derive the perturbation equations appropriate for the MC SCF theory. Since the perturbation theory in the traditional HF method can be written down in both the finite field [9] and the analytic (CHF) [4] form, we aim to obtain the MC SCF equivalent of the CHF scheme of Stevens, Pitzer and Lipscomb [4].

The analytic form of the CHF method [4] provides a very convenient starting point for the discussion of several approximations [3, 4, 10–15, 44]. The contributions to the corresponding *n*th order perturbed energy can be given some physical interpretation [14] hardly available in the finite field approach. We hope that to some extent these features of the analytic approach will be also valuable for the MC SCF perturbation theory.

We shall confine our considerations to the closed-shell systems. Then, the MC SCF scheme of Clementi and Veillard [34] seems to be the most appropriate for the derivation of the relevant perturbation equations. Since there is a close correspondence of the MC SCF equations of Clementi and Veillard [34] and those of the traditional HF theory [39, 45], a similar relation should hold for the perturbation theories for these methods. As a consequence, our derivation of the MC SCF perturbation equations follows the technique used by Lipscomb [4, 16]. However, some attention is given to the variational formulation of the solution of the perturbation equations. This provides a convenient computational framework for the calculation of the perturbed orbitals and energies. The derivations reported in this paper are limited to the first-order perturbed equations and the second-order energy formula. The extension to higher orders of the perturbation theory is straightforward.

2. Basic Definitions

In order to avoid the unnecessary repetitions we shall completely follow the conventions and notation of Clementi and Veillard [34]. However, in the present case the total Hamiltonian of the $2n$-electron closed shell system is given by

$$\mathscr{H} = \mathscr{H}^{(0)} + \lambda \mathscr{H}^{(1)} \tag{1}$$

where $\mathscr{H}^{(0)}$ is the unperturbed Hamiltonian and the perturbation $\mathscr{H}^{(1)}$ is assumed to be a sum of one-electron operators

$$\mathscr{H}^{(1)} = \sum_{k=1}^{2n} \mathscr{h}^{(1)}(k) \tag{2}$$

Thus the total one-electron part of (1) can be written as

$$\sum_{k=1}^{2n} \mathscr{h}(k) = \sum_{k=1}^{2n} (\mathscr{h}^{(0)}(k) + \lambda \mathscr{h}^{(1)}(k)). \tag{3}$$

According to Clementi and Veillard the MC SCF wave function

$$\Psi = a_{00}\Phi_{00} + \sum_{t=1}^{n} \sum_{u=n+1}^{m} a_{tu}\Phi_{tu} \tag{4}$$

corresponding to the Hamiltonian (1) will now depend on the perturbation $\mathscr{H}^{(1)}$ via both the linear parameters a_{00}, a_{tu} and the MC SCF orbitals t, u. The perturbation-dependent average electronic energy is in this approximation given by [34]:

$$\begin{aligned} E = {} & a_{00}^{*}a_{00}E_{00} + \sum_{t=1}^{n} \sum_{u=n+1}^{m} a_{tu}^{*}a_{tu}E_{tu} \\ & + \sum_{t=1}^{n} \sum_{u=n+1}^{m} \sum_{t'=1}^{n} \sum_{u'=n+1}^{m} a_{tu}^{*}a_{t'u'} \\ & \times [K_{tt'}\delta_{uu'}(1-\delta_{tt'}) + K_{uu'}\delta_{tt'}(1-\delta_{uu'})] \\ & + \sum_{t=1}^{n} \sum_{u=n+1}^{m} (a_{00}^{*}a_{tu} + a_{00}a_{tu}^{*})K_{tu} \end{aligned} \tag{5}$$

provided the following orthogonality conditions are satisfied

$$a_{00}^{*}a_{00} + \sum_{t=1}^{n} \sum_{u=n+1}^{m} a_{tu}^{*}a_{tu} = 1 \tag{6}$$

$$\langle i | j \rangle = \delta_{ij} \tag{7}$$

with i, j denoting any of the t- or u-type MC SCF orbitals.

Assuming that the expansion of all the relevant quantities in terms of the perturbation parameter λ at λ close to zero, is valid, we get

$$\Psi = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \cdots \tag{8a}$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots \tag{8b}$$

$$a_{00} = a_{00}^{(0)} + \lambda a_{00}^{(1)} + \lambda^2 a_{00}^{(2)} + \cdots \tag{8c}$$

$$a_{tu} = a_{tu}^{(0)} + \lambda a_{tu}^{(1)} + \lambda^2 a_{tu}^{(2)} + \cdots \tag{8d}$$

$$|i\rangle = |i^{(0)}\rangle + \lambda|i^{(1)}\rangle + \lambda^2|i^{(2)}\rangle + \cdots \tag{8e}$$

where (8e) refers to any orbital entering the determinants in (4). The expansions (8c)–(8e) lead to the following orthogonality conditions

$$a_{00}^{(0)*}a_{00}^{(0)} + \sum_{t=1}^{n}\sum_{u=n+1}^{m} a_{tu}^{(0)*}a_{tu}^{(0)} = 1 \tag{9a}$$

$$a_{00}^{(1)*}a_{00}^{(0)} + a_{00}^{(0)*}a_{00}^{(1)} + \sum_{t=1}^{n}\sum_{u=n+1}^{m} (a_{tu}^{(1)*}a_{tu}^{(0)} + a_{tu}^{(0)*}a_{tu}^{(1)}) = 0 \tag{9b}$$

$$a_{00}^{(2)*}a_{00}^{(0)} + a_{00}^{(1)*}a_{00}^{(1)} + a_{00}^{(0)*}a_{00}^{(2)} + \sum_{t=1}^{n}\sum_{u=n+1}^{m} (a_{tu}^{(2)*}a_{tu}^{(0)} + a_{tu}^{(1)*}a_{tu}^{(1)} + a_{tu}^{(0)*}a_{tu}^{(2)}) = 0 \tag{9c}$$

and

$$\langle i^{(0)}|j^{(0)}\rangle = \delta_{ij} \tag{10a}$$

$$\langle i^{(1)}|j^{(0)}\rangle + \langle i^{(0)}|j^{(1)}\rangle = 0 \tag{10b}$$

$$\langle i^{(2)}|j^{(0)}\rangle + \langle i^{(1)}|j^{(1)}\rangle + \langle i^{(0)}|j^{(2)}\rangle = 0 \tag{10c}$$

resulting from the zeroth-, first-, and the second-order terms of Eq. (6) and Eq. (7), respectively. Provided the conditions (6) and (7) are satisfied, Eq. (5) represents the total energy functional

$$J = J[a_{00}, a_{tu}, |i\rangle] \tag{11}$$

with the following expansion

$$J = J^{(0)} + \lambda J^{(1)} + \lambda^2 J^{(2)} + \cdots \tag{12}$$

The extremization of $J^{(0)}$ with respect to $a_{00}^{(0)}$, $a_{tu}^{(0)}$, and $|i^{(0)}\rangle$ leads to the unperturbed MC SCF equations given by Clementi and Veillard [34]:

$$\begin{aligned}
&(E_{00}^{(0)} - E^{(0)})a_{00}^{(0)} + \sum_{t=1}^{n}\sum_{u=n+1}^{m} a_{tu}^{(0)}K_{tu}^{(0)} = 0\\
&(E_{tu}^{(0)} - E^{(0)})a_{tu}^{(0)} + a_{00}^{(0)}K_{tu}^{(0)}\\
&\qquad + \sum_{t'=1}^{n}\sum_{u'=n+1}^{m} a_{t'u'}^{(0)}(K_{tt'}^{(0)}\delta_{uu'} + K_{uu'}^{(0)}\delta_{tt'})(1 - \delta_{uu'}\delta_{tt'}) = 0
\end{aligned} \tag{13}$$

and

$$
\begin{aligned}
F_t^{(0)}|t^{(0)}\rangle &= \sum_{i=1}^{m} \vartheta_{ti}^{(0)}|i^{(0)}\rangle \\
F_u^{(0)}|u^{(0)}\rangle &= \sum_{i=1}^{m} \vartheta_{ui}^{(0)}|i^{(0)}\rangle
\end{aligned}
\tag{14}
$$

where $E^{(0)}$ and $\vartheta_{kl}^{(0)}$ represent the appropriate Lagrangian multipliers. The operators $F_t^{(0)}$ and $F_u^{(0)}$ are those defined by Eqs. (19a) and (19b) of Ref. [34] but written down for the zeroth-order coefficients and orbitals.

From now on we assume that the zeroth-order MC SCF equations have been exactly[1] solved. Under these conditions it can be easily shown that the first-order functional $J^{(1)}$ does not in fact depend on the first-order coefficients and the first-order orbitals. Thus $J^{(1)}$ is reduced to the first-order perturbed energy formula

$$
J^{(1)} = E^{(1)} = 2 \sum_{i=1}^{m} P^{(0)}(i)\langle i^{(0)}|h^{(1)}|i^{(0)}\rangle \tag{15}
$$

and does not provide any variation principle. For the sake of convenience we introduced in Eq. (15) the notation proposed by Gołębiewski and Nowak-Brocławik [39]

$$
P^{(0)}(i) = \begin{cases} 1 - A_t^{(0)} & \text{for } i = t \\ B_u^{(0)} & \text{for } i = u \end{cases} \tag{16}
$$

where according to Eq. (9b) and (10b) of Ref. [16]

$$
A_t^{(0)} = \sum_{u=n+1}^{m} a_{tu}^{(0)*} a_{tu}^{(0)} \tag{17a}
$$

$$
B_u^{(0)} = \sum_{t=1}^{n} a_{tu}^{(0)*} a_{tu}^{(0)} \tag{17b}
$$

Equation (15) is quite obvious for the first-order perturbation theory [46] and closely resembles that found in the traditional HF scheme [4]. It simply confirms the statement known as the generalized Hellmann-Feynman theorem for the MC SCF wave functions [47].

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[1] By the exact solution we understand also any solution of the MC SCF equations obtained within the finite basis set approximation. In order to preserve the bounding properties of the higher-order functionals this basis set cannot be extended when considering the perturbed orbitals. Then, although

$$
\mathscr{F}_i^{(0)}|i^{(0)}\rangle = \sum_{j=1}^{m} \vartheta_{ij}^{(0)}|j^{(0)}\rangle + \chi
$$

the function χ will be orthogonal to all the orbitals.

The second-order energy functional $J^{(2)}$ will depend in general on the first-order as well as on the second-order perturbed coefficients and orbitals. Collecting the appropriate terms of the expansion of the total functional, we obtain

$$J^{(2)}=J^{(2)}[a_{00}^{(1)}, a_{00}^{(2)}, a_{tu}^{(1)}, a_{tu}^{(2)}, |i^{(1)}\rangle, |i^{(2)}\rangle]=J_{aa}^{(2)}+J_{ab}^{(2)}+J_{bb}^{(2)} \tag{18}$$

where

$$\begin{aligned}
J_{aa}^{(2)}&=J_{aa}^{(2)}[a_{00}^{(1)}, a_{00}^{(2)}, a_{tu}^{(1)}, a_{tu}^{(2)}]\\
&=(a_{00}^{(2)*}a_{00}^{(0)}+a_{00}^{(1)*}a_{00}^{(1)}+a_{00}^{(0)*}a_{00}^{(2)})E_{00}^{(0)}\\
&\quad+\sum_{t=1}^{n}\sum_{u=n+1}^{m}(a_{tu}^{(2)*}a_{tu}^{(0)}+a_{tu}^{(1)*}a_{tu}^{(1)}+a_{tu}^{(0)*}a_{tu}^{(2)})E_{tu}^{(0)}\\
&\quad+\sum_{t=1}^{n}\sum_{u=n+1}^{m}\sum_{t'=1}^{n}\sum_{u'=n+1}^{m}(a_{tu}^{(2)*}a_{t'u'}^{(0)}+a_{tu}^{(1)*}a_{t'u'}^{(1)}+a_{tu}^{(0)*}a_{t'u'}^{(2)})\\
&\quad\times(K_{tt'}^{(0)}\delta_{uu'}+K_{uu'}^{(0)}\delta_{tt'})(1-\delta_{tt'}\delta_{uu'})\\
&\quad+\sum_{t=1}^{n}\sum_{u=n+1}^{m}(a_{00}^{(2)*}a_{tu}^{(0)}+a_{00}^{(1)*}a_{tu}^{(1)}+a_{00}^{(0)*}a_{tu}^{(2)}+a_{00}^{(2)}a_{tu}^{(0)*}\\
&\quad+a_{00}^{(1)}a_{tu}^{(1)*}+a_{00}^{(0)}a_{tu}^{(2)*})K_{tu}^{(0)}
\end{aligned} \tag{19a}$$

$$\begin{aligned}
J_{ab}^{(2)}&=J_{ab}^{(2)}[a_{00}^{(1)}, a_{tu}^{(1)}, |i^{(1)}\rangle]\\
&=(a_{00}^{(1)*}a_{00}^{(0)}+a_{00}^{(0)*}a_{00}^{(1)})E_{00}^{(1)}\\
&\quad+\sum_{t=1}^{n}\sum_{u=n+1}^{m}(a_{tu}^{(1)*}a_{tu}^{(0)}+a_{tu}^{(0)*}a_{tu}^{(1)})E_{tu}^{(1)}\\
&\quad+\sum_{t=1}^{n}\sum_{u=n+1}^{m}\sum_{t'=1}^{n}\sum_{u'=n+1}^{m}(a_{tu}^{(1)*}a_{t'u'}^{(0)}+a_{tu}^{(0)*}a_{t'u'}^{(1)})\\
&\quad\times(K_{tt'}^{(1)}\delta_{uu'}+K_{uu'}^{(1)}\delta_{tt'})(1-\delta_{tt'}\delta_{uu'})\\
&\quad+\sum_{t=1}^{n}\sum_{u=n+1}^{m}(a_{00}^{(1)*}a_{tu}^{(0)}+a_{00}^{(0)*}a_{tu}^{(1)}+a_{00}^{(1)}a_{tu}^{(0)*}+a_{00}^{(0)}a_{tu}^{(1)*})K_{tu}^{(1)}
\end{aligned} \tag{19b}$$

$$\begin{aligned}
J_{bb}^{(2)}&=J_{bb}^{(2)}[|i^{(1)}\rangle, |i^{(2)}\rangle]\\
&=a_{00}^{(0)*}a_{00}^{(0)}E_{00}^{(2)}+\sum_{t=1}^{n}\sum_{u=n+1}^{m}a_{tu}^{(0)*}a_{tu}^{(0)}E_{tu}^{(2)}\\
&\quad+\sum_{t=1}^{n}\sum_{u=n+1}^{m}\sum_{t'=1}^{n}\sum_{u'=n+1}^{m}a_{tu}^{(0)*}a_{t'u'}^{(0)}(K_{tt'}^{(2)}\delta_{uu'}+K_{uu'}^{(2)}\delta_{tt'})\\
&\quad\times(1-\delta_{tt'}\delta_{uu'})\\
&\quad+\sum_{t=1}^{n}\sum_{u=n+1}^{m}(a_{00}^{(0)*}a_{tu}^{(0)}+a_{00}^{(0)}a_{tu}^{(0)*})K_{tu}^{(2)}
\end{aligned} \tag{19c}$$

In these formulae $E_{00}^{(0)}$, $E_{00}^{(1)}$, $E_{00}^{(2)}$, $E_{tu}^{(0)}$, $E_{tu}^{(1)}$, $E_{tu}^{(2)}$, and $K_{tu}^{(0)}$, $K_{tu}^{(1)}$, $K_{tu}^{(2)}$ correspond to the appropriate orders of the perturbation expansion of E_{00}, E_{tu} and K_{tu}, respectively (see Eqs. (3) and (4) of Ref. [34]). It is worth attention that these quantities do not involve the variation coefficients. It will be shown in the next

Section that assuming the knowledge of the exact solution of the unperturbed MC SCF problem and the orthogonality conditions (9c) and (10c) we can simplify the functional (18) to the form containing only the first-order perturbed coefficients and orbitals. One can also generally prove that the functional (18) including the second-order coefficients and orbitals, gives the exact upper bound to the second-order energy.

3. The Second-Order MC SCF Perturbation Theory

Collecting the terms of $J_{aa}^{(2)}$ which contain either $a_{00}^{(2)*}$ and $a_{tu}^{(2)*}$ or their complex conjugates and using both Eq. (13) and Eq. (9c) we obtain without any approximation the following result

$$\begin{aligned} J_{aa}^{(2)} &= J_{aa}^{(2)}[a_{00}^{(1)}, a_{tu}^{(1)}] \\ &= a_{00}^{(1)*}(E_{00}^{(0)} - E^{(0)})a_{00}^{(1)} + a_{00}^{(1)*} \sum_{t=1}^{n} \sum_{u=n+1}^{m} a_{tu}^{(1)} K_{tu}^{(0)} \\ &\quad + a_{00}^{(1)} \sum_{t=1}^{n} \sum_{u=n+1}^{m} a_{tu}^{(1)*} K_{tu}^{(0)} + \sum_{t=1}^{n} \sum_{u=n+1}^{m} a_{tu}^{(1)*}(E_{tu}^{(0)} - E^{(0)})a_{tu}^{(1)} \\ &\quad + \sum_{t=1}^{n} \sum_{u=n+1}^{m} \sum_{t'=1}^{n} \sum_{u'=n+1}^{m} a_{tu}^{(1)*} a_{t'u'}^{(1)} (K_{tt'}^{(0)} \delta_{uu'} + K_{uu'}^{(0)} \delta_{tt'})(1 - \delta_{tt'}\delta_{uu'}) \end{aligned} \tag{20}$$

Thus, so far as the number of determinants in (4) is the same for both the perturbed and the unperturbed problem, the second-order energy functional will not involve the second-order perturbed coefficients.

It is also desirable to remove the second-order perturbed orbitals from the functional $J_{bb}^{(2)}$. The procedure, although tedious, is still straightforward. However, when dropping the terms containing $|i^{(2)}\rangle$ or $\langle i^{(2)}|$ we must assume that the exact solution of the integro-differential equations (14) is known or that the second-order perturbed orbitals are determined in the same basis set as $|i^{(0)}\rangle$ and $|i^{(1)}\rangle$ (see also Footnote 1). Accepting rather the last assumption, i.e., fixing the basis set, and using the orthogonality conditions (10c), we finally obtain

$$\begin{aligned} J_{bb}^{(2)} &= J_{bb}^{(2)}[|i^{(1)}\rangle] \\ &= \sum_{i=1}^{m} \Bigg[2 \sum_{j=1}^{m} \langle i^{(1)} | \mathscr{F}_i^{(0)} \delta_{ij} - \vartheta_{ij}^{(0)} | j^{(1)} \rangle \\ &\qquad + \langle i^{(1)} | \mathscr{F}_{i,b}^{(1)} | i^{(0)} \rangle + \langle i^{(0)} | \mathscr{F}_{i,b}^{(1)} | i^{(1)} \rangle \\ &\qquad + P^{(0)}(i)(\langle i^{(1)} | \mathscr{h}^{(1)} | i^{(0)} \rangle + \langle i^{(0)} | \mathscr{h}^{(1)} | i^{(1)} \rangle) \Bigg] \end{aligned} \tag{21}$$

where

$$\mathscr{F}_{i,b}^{(1)}=\begin{cases} (1-A_t^{(0)})\mathscr{h}^{(1)}+2\sum\limits_{t'=1}^{n}(1-A_t^{(0)}-A_{t'}^{(0)})P_{t'}^{(1)} \\ \quad +2A_t^{(0)}P_t^{(1)}+2\sum\limits_{u=n+1}^{m}B_u^{(0)}P_u^{(1)} \\ \quad +\sum\limits_{u=n+1}^{m}[(a_{00}^{(0)*}a_{tu}^{(0)}+a_{00}^{(0)}a_{tu}^{(0)*})\frac{1}{2}K_u^{(1)}-2a_{tu}^{(0)*}a_{tu}^{(0)}P_u^{(1)}] \\ \quad +\sum\limits_{t'=1}^{n}A_{tt'}^{(0)}K_{t'}^{(1)}(1-\delta_{tt'}) \quad \text{for } i=t \\ \text{and} \\ B_u^{(0)}(\mathscr{h}^{(1)}+2P_u^{(1)}+\sum\limits_{t=1}^{n}2P_t^{(1)}) \\ \quad +\sum\limits_{t=1}^{n}[\frac{1}{2}(a_{00}^{(0)*}a_{tu}^{(0)}+a_{00}^{(0)}a_{tu}^{(0)*})K_t^{(1)}-2a_{tu}^{(0)*}a_{tu}^{(0)}P_t^{(1)}] \\ \quad +\sum\limits_{u'=n+1}^{m}B_{uu'}^{(0)}K_{u'}^{(1)}(1-\delta_{uu'}) \quad \text{for } i=u \end{cases} \tag{22}$$

corresponds to the part of the first-order expansion of $\mathscr{F}_i$, which does not involve the first-order perturbed coefficients. The first-order perturbed operators appearing in (22) can be easily derived by the expansion of the appropriate formulae given in Ref. [34]. The same applies to $A_{tt'}^{(0)}$ and $B_{uu'}^{(0)}$.

Passing from the functional (19c) to the functional (21) violates the exact bounding properties of (18). The functional in which the $J_{bb}^{(2)}$ part is replaced by (21) will give the second-order energy upper bound for a given zeroth-order MC SCF wave function. But even these bounding properties will be violated if the first-order perturbed orbitals do not refer to the basis set adopted for $|i^{(0)}\rangle$ [15, 48, 49]. In some cases this may result in a rather inconvenient restriction of the variation-perturbation approach.

Before deriving the first-order perturbation equations it is useful to re-write the $J_{ab}^{(2)}$ part of (18) in the form which explicitly shows the dependence on the first-order perturbed orbitals

$$J_{ab}^{(2)}=\sum_{i=1}^{m}[\langle i^{(1)}|\mathscr{F}_{i,a}^{(1)}|i^{(0)}\rangle+\langle i^{(0)}|\mathscr{F}_{i,a}^{(1)}|i^{(1)}\rangle \\ +P^{(1)}(i)\langle i^{(0)}|\mathscr{h}^{(1)}|i^{(0)}\rangle] \tag{23}$$

where

$$P^{(1)}(i)=\begin{cases} -A_t^{(1)} & \text{for } i=t \\ B_u^{(1)} & \text{for } i=u \end{cases} \tag{24}$$

and

$$\mathscr{F}_{i,a}^{(1)} = \begin{cases} -A_t^{(1)}\hbar^{(0)} - 2\sum\limits_{t'=1}^{n}(A_t^{(1)} + A_{t'}^{(1)})P_{t'}^{(0)} \\ +2A_t^{(1)}P_t^{(0)} + 2\sum\limits_{u=n+1}^{m} B_u^{(1)}P_u^{(0)} \\ +\sum\limits_{u=n+1}^{m}[\tfrac{1}{2}(a_{00}^{(1)*}a_{tu}^{(0)} + a_{00}^{(0)*}a_{tu}^{(1)} + a_{00}^{(1)}a_{tu}^{(0)*} + a_{00}^{(0)}a_{tu}^{(1)*}(K_u^{(0)} \\ -2(a_{tu}^{(1)*}a_{tu}^{(0)} + a_{tu}^{(0)*}a_{tu}^{(1)})P_u^{(0)}] + \sum\limits_{t'=1}^{n} A_{tt'}^{(1)}K_{t'}^{(0)}(1-\delta_{tt'}) \quad \text{for } i=t, \\ \text{and} \\ B_u^{(1)}(\hbar^{(0)} + 2P_u^{(0)} + \sum\limits_{t=1}^{n} 2P_t^{(0)}) \\ +\sum\limits_{t=1}^{n}[\tfrac{1}{2}(a_{00}^{(1)*}a_{tu}^{(0)} + a_{00}^{(0)*}a_{tu}^{(1)} + a_{00}^{(1)}a_{tu}^{(0)*} + a_{00}^{(0)}a_{tu}^{(1)*})K_t^{(0)} \\ -2(a_{tu}^{(1)*}a_{tu}^{(0)} + a_{tu}^{(0)*}a_{tu}^{(1)})P_t^{(0)}] \\ +\sum\limits_{u'=n+1}^{m} B_{uu'}^{(1)}K_{u'}^{(0)}(1-\delta_{uu'}) \quad \text{for } i=u \end{cases} \tag{25}$$

is the counterpart of $\mathscr{F}_{i,b}^{(1)}$ but involving only the first-order perturbed coefficients.

The variation of the total functional, expressed either as a sum of Eqs. (20), (19b) and (19c) or as a sum of Eqs. (20), (23) and (21) with respect to the first-order perturbed coefficients and the first-order perturbed orbitals, respectively, is constrained by the orthgonality requirements (9b) and (10b). Including these constraints via the appropriate Lagrangian multipliers and performing the variation of the relevant form of the functional, we obtain the first-order perturbed MC SCF equations:

$$\begin{aligned} &(E_{00}^{(0)} - E^{(0)})a_{00}^{(1)} + \sum_{t=1}^{n}\sum_{u=n+1}^{m} a_{tu}^{(1)}K_{tu}^{(0)} \\ &\quad = -(E_{00}^{(1)} - E^{(1)})a_{00}^{(0)} - \sum_{t=1}^{n}\sum_{u=n+1}^{m} a_{tu}^{(0)}K_{tu}^{(1)} \\ &(E_{tu}^{(0)} - E^{(0)})a_{tu}^{(1)} + a_{00}^{(1)}K_{tu}^{(0)} + \sum_{t'=1}^{n}\sum_{u'=n+1}^{m} a_{t'u'}^{(1)}(K_{tt'}^{(0)}\delta_{uu'} + K_{uu'}^{(0)}\delta_{tt'}) \\ &\quad \times (1-\delta_{tt'}\delta_{uu'}) \\ &\quad = -(E_{tu}^{(1)} - E^{(1)})a_{tu}^{(0)} - a_{00}^{(0)}K_{tu}^{(1)} \\ &\qquad - \sum_{t'=1}^{n}\sum_{u'=n+1}^{m} a_{t'u'}^{(0)}(K_{tt'}^{(1)}\delta_{uu'} + K_{uu'}^{(1)}\delta_{tt'})(1-\delta_{tt'}\delta_{uu'}) \end{aligned} \tag{26}$$

for the first-order perturbed coefficients, and

$$\begin{aligned}(\mathscr{F}_i^{(0)}-\vartheta_{ii}^{(0)})|i^{(1)}\rangle-\sum_{j\neq i}^{m}\vartheta_{ij}^{(0)}|j^{(1)}\rangle\\ =-(\mathscr{F}_i^{(1)}-\vartheta_{ii}^{(1)})|i^{(0)}\rangle+\sum_{j\neq i}^{m}\vartheta_{ij}^{(1)}|j^{(0)}\rangle\end{aligned} \tag{27}$$

for the first-order perturbed orbitals. Both $E^{(1)}$ and $\vartheta_{ij}^{(1)}$ arise from the corresponding Lagrangian multipliers by a subsequent comparison with the formal expansion of Eqs. (29), (30), (22a) and (22b) of Clementi and Veillard [34]. The operator $\mathscr{F}_i^{(1)}$ is defined by

$$\mathscr{F}_i^{(1)}=\mathscr{F}_{i,a}^{(1)}+\mathscr{F}_{i,b}^{(1)} \tag{28}$$

and represents the total first-order perturbed MC SCF one-electron operator.

Before passing to the discussion of the first-order perturbed MC SCF equations (26) and (27) let us assume that their solution minimizing the corresponding second-order energy functional, is known. The value of the functional calculated for these solutions becomes the second-order energy formula for the MC SCF scheme. Thus

$$\begin{aligned}\min J^{(2)}&=E^{(2)}\\ &=\sum_{i=1}^{m}[P^{(1)}(i)\langle i^{(0)}|\mathscr{h}^{(1)}|i^{(0)}\rangle\\ &\quad+P^{(0)}(i)(\langle i^{(1)}|\mathscr{h}^{(1)}|i^{(0)}\rangle+\langle i^{(0)}|\mathscr{h}^{(1)}|i^{(1)}\rangle)]\end{aligned} \tag{29}$$

and has a direct physical interpretation. The first term involving $P^{(1)}(i)$ represents the contribution to $E^{(2)}$ due to a change of the occupation numbers of the electron-pair levels. The other terms refer to the effect of the perturbation upon the orbitals. Both, $P^{(1)}(i)$ and $|i^{(1)}\rangle$ are in fact coupled by the mutual dependence of the solutions of Eqs. (26) and (27). Moreover, the second-order energy formula (29) can be easily reduced to that for the one-determinantal form of (4). In this case

$$P^{(1)}(i)\equiv 0$$

and

$$P^{(0)}(i)=\begin{cases}1 & \text{for } i=t\\ 0 & \text{for } i=u\end{cases}$$

Thus

$$E^{(2)}=\sum_{t=1}^{h}(\langle t^{(1)}|\mathscr{h}^{(1)}|t^{(0)}\rangle+\langle t^{(0)}|\mathscr{h}^{(1)}|t^{(1)}\rangle)$$

and one recognizes the well-known second-order energy formula of the CHF scheme [4, 16].

It follows also that in the one-configuration approximation of $\Psi^{(0)}$ both $\mathscr{F}_t^{(0)}$ and $\mathscr{F}_t^{(1)}$ become independent of t and can be written as $\mathscr{F}^{(0)}$ and $\mathscr{F}^{(1)}$, respectively. Moreover, if we assume that the unperturbed orbitals $|t^{(0)}\rangle$ were chosen in the so-called canonical form [50], the first-order perturbed orbital equation reads

$$(\mathscr{F}^{(0)}-\vartheta_{tt}^{(0)})|t^{(1)}\rangle=-(\mathscr{F}^{(1)}-\vartheta_{tt}^{(1)})|t^{(0)}\rangle+\sum_{t'\neq t}^{n}\vartheta_{tt'}^{(1)}|t'^{(0)}\rangle \tag{30}$$

and is completely equivalent to that derived in the CHF perturbation theory[2]. Thus, the reduction of Eq. (27) to the first-order perturbed CHF equation clearly shows that the present scheme is a natural extension of the ordinary HF perturbation theory.

Apparently, the perturbation equations of this paper are confined to the closed-shell systems representable by the MC SCF wave function of the form (4). Their generalization for a more complete form of the MC SCF wave function [37, 51] is straightforward but requires a rather cumbersome notation. Except for increasing complexity, the use of more general functions does not raise any new formal or computational problems. It should also be pointed out that in the case of open-shell systems the present approach is equivalent to that of Diercksen and McWeeny [52].

4. Remarks on the Computational Scheme for the Solution of the First-Order Perturbed MC SCF Equations

It is worth attention that the perturbed MC SCF equations (26) and (27) are mutually coupled due to a simultaneous presence of both the perturbed coefficients $a_{00}^{(1)}$, $a_{tu}^{(1)}$ and the perturbed orbitals $|i^{(1)}\rangle$. Hence, their solution will require some iterative approach which allows to treat them separately.

The analysis of the relative importance of the perturbed coefficients and orbitals [3] leads to the conclusion that in the zeroth iteration one can assume

$$a_{00}^{(1)}=a_{tu}^{(1)}=0$$

and begin with the solution of Eq. (27) for the zeroth approximation to the first-order perturbed orbitals. These are substituted into Eq. (26) and lead to the next approximation for the perturbed coefficients. The iterations are repeated until the solutions become selfconsistent.

Since the solution of Eq. (26) with already known perturbed orbitals $|i^{(1)}\rangle$ is completely straightforward, we shall focus our attention on the first-order perturbed orbital equations (27). For this purpose we shall assume that all the terms

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[2] Since the components of $|t^{(1)}\rangle$ involving the occupied unperturbed orbitals do not contribute to the second-order CHF energy [4], one usually neglects the off-diagonal first-order Lagrangian multipliers $\vartheta_{tt'}^{(1)}$.

[3] For instance, in a number of cases $a_{00}^{(1)}=a_{tu}^{(1)}=0$ by symmetry. It is also known that the CHF scheme accounts for a major portion of the second-order perturbed energies, indicating that the orbital perturbations are the most important ones. Thus the first term of Eq. (29) gives a rather small contribution and can be neglected in the zeroth approximation.

contributing to $\mathscr{F}_{i,a}^{(1)}$, i.e., the terms involving the perturbed coefficients, are known. However, one finds that the corresponding equations are still coupled via the perturbation of the one-electron MC SCF potential. Since this potential is determined by all the unknown perturbed orbitals, the most convenient approach to the solution of Eqs. (27) will require another iterative scheme.

It should be pointed out that in the ordinary CHF scheme both the iterative approach [14] and the method based on the direct solution of the set of linear equations [4, 18] (see also [53]) are currently in use. In principle both these methods can be also applied in the present case. However, because of the presence of the off-diagonal Lagrangian multipliers, the iterative approach seems to be more convenient.

In order to define the iterative scheme for the solution of Eqs. (27) one has to choose the appropriate zeroth approximation for the perturbed orbitals contributing to the r.h.s. In the CHF scheme this procedure is known as the uncoupling of the CHF equations [4, 14, 44] and quite frequently the uncoupled solution (zeroth approximation of the iterative scheme) is fairly close to the exact one [12, 44, 53, 54]. The same idea seems to be applicable also in the case of the MC SCF perturbed orbital equations.

Let us express the perturbation operator $\mathscr{F}_i^{(1)}$ in the form

$$\mathscr{F}_i^{(1)} = P^{(0)}(i)\mathscr{h}^{(1)} + \mathscr{F}_{i,a}^{(1)} + \mathscr{F}_{i,bi}^{(1)} + \sum_{j\neq i}^{m} \mathscr{F}_{i,bj}^{(1)} \tag{31}$$

where $\mathscr{F}_{i,bi}^{(1)}$ contains all the terms involving $|i^{(1)}\rangle$ and the other perturbed orbitals $|j^{(1)}\rangle \neq |i^{(1)}\rangle$ contribute to the last term of Eq. (31). $P^{(0)}(i)$ [39] is equal either $1 - A_t^{(0)}(i=t)$ or $B_u^{(0)}(i=u)$. The experience gained in the CHF calculations [4, 14, 44] shows that a very convenient zeroth approximation is obtained by neglecting all the terms involving $|j^{(1)}\rangle \neq |i^{(1)}\rangle$. Applying the same idea in the present case we find that the uncoupled solutions for $|i^{(1)}\rangle$ are determined by

$$\begin{aligned}(\mathscr{F}_i^{(0)} - \vartheta_{ii}^{(0)})|i^{(1)}\rangle + \mathscr{F}_{i,bi}^{(1)}|i^{(0)}\rangle \\ = -(\mathscr{F}_{i,a}^{(1)} + P^{(0)}(i)\mathscr{h}^{(1)} - \vartheta_{ii}^{(1)})|i^{(0)}\rangle + \sum_{j\neq i}^{m} \vartheta_{ij}^{(1)}|j^{(0)}\rangle\end{aligned} \tag{32}$$

It should be noticed that Eq. (32) represents the MC SCF counterpart of the so-called UCHF Method b′ of Langhoff, Karplus and Hurst [7]. However, in the present case the uncoupling of Eq. (27) involves also the neglect of the terms coupled through the off-diagonal Lagrangian multipliers $\vartheta_{ij}^{(0)}$.

By analogy with the uncoupling procedures in the CHF scheme one can say that Eq. (32) contains the so-called self-coupling terms ($\mathscr{F}_{i,bi}^{(1)}$) [7]. Neglecting them, we obtain the most approximate uncoupled MC SCF perturbation equations of the form

$$(\mathscr{F}_i^{(0)} - \vartheta_{ii}^{(0)})|i^{(1)}\rangle = -(\mathscr{F}_{i,a}^{(1)} + P^{(0)}(i)\mathscr{h}^{(1)} - \vartheta_{ii}^{(1)})|i^{(0)}\rangle + \sum_{j\neq i}^{m} \vartheta_{ij}^{(1)}|j^{(0)}\rangle \tag{33}$$

They can be considered as the MC SCF equivalent of the Dalgarno uncoupled scheme [3, 7, 12].

Similarly as in the case of the CHF method one can devise a variety of the uncoupling procedures [7, 12] differing by the retained portion of the self-coupling terms. The corresponding orbital solutions can be used either as a subsequent approximation for the r.h.s. of Eq. (27) or as the final uncoupled MC SCF result. For any of these uncoupled schemes one can use the result of the next iterative solution of Eqs. (27) to compute the corresponding "first-order" [55] correction to the uncoupled value of the second-order energy. A further improvement of the uncoupled second-order energies is possible by utilizing the so-called geometric approximation [44, 56, 57, 58] derived from the corresponding variational principle [57].

Usually in order to solve integro-differential equations like Eq. (32) or Eq. (33) the algebraic techniques are utilized [4, 14]. Following the methods employed in the CHF scheme [4, 14, 18] we shall assume that each $|i^{(1)}\rangle$ is expandable into a set of the unperturbed MC SCF orbitals

$$|i^{(1)}\rangle = \sum_{j\neq i}^{m} c_{ij}|j^{(0)}\rangle + \sum_{r=m+1} c_{ir}|r^{(0)}\rangle \tag{34}$$

where the second sum involves the so-called hypervirtual orbitals [39]. The set $\{|j^{(0)}\rangle, |r^{(0)}\rangle\}$ is assumed to be orthonormal. With the expansion (34) the orthogonality conditions (10b) can be written as

$$c_{ik} + c_{ki}^{*} = 0 \tag{35}$$

Thus

$$c_{ik} = \mp c_{ki} \tag{36}$$

where the upper or lower sign refers to real or pure imaginary perturbation, respectively. It follows also that without loss of generality we can put

$$c_{ii} = 0 \tag{37}$$

confirming the validity of the neglect of the corresponding term in Eq. (34).

Substituting Eq. (34) into Eq. (32) and projecting the result onto $\langle \ell^{(0)}| \neq \langle i^{(0)}|$ one finally obtains the following set of algebraic equations for the determination of the unknown expansion coefficients

$$\begin{aligned}\sum_{k\neq i}^{\mathrm{M}} c_{ik}\{\langle \ell^{(0)}|\mathscr{F}_{i}^{(0)}|k^{(0)}\rangle + P^{(0)}(i)(2\langle \ell^{(0)}i^{(0)}|i^{(0)}k^{(0)}\rangle \\ \pm\langle \ell^{(0)}k^{(0)}|i^{(0)}i^{(0)}\rangle - \langle \ell^{(0)}i^{(0)}|k^{(0)}i^{(0)}\rangle) - \vartheta_{ii}^{(0)}\delta_{lk}\} \\ = -\langle \ell^{(0)}|\mathscr{F}_{i,a}^{(1)} + P^{(0)}(i)\hbar^{(1)}|i^{(0)}\rangle + \sum_{j\neq i}^{m} \vartheta_{ij}^{(1)}\delta_{lj}\end{aligned} \tag{32a}$$

where

$$\langle i^{(0)}j^{(0)}|k^{(0)}l^{(0)}\rangle = \iint i^{(0)*}(1)j^{(0)*}(2)r_{12}^{-1}k^{(0)}(1)l^{(0)}(2)dv_1dv_2$$

and M denotes the dimension of the basis set of the unperturbed MC SCF orbitals.

The same technique applied to Eq. (33) results in

$$\sum_{k\neq i}^{\mathrm{M}} c_{ik}(\langle \ell^{(0)}|\mathscr{F}_i^{(0)}|k^{(0)}\rangle - \vartheta_{ii}^{(0)}\delta_{lk}) = -\langle \ell^{(0)}|\mathscr{F}_{i,a}^{(1)} + P^{(0)}(i)\mathscr{h}^{(1)}|i^{(0)}\rangle + \sum_{j\neq i}^{m} \vartheta_{ij}^{(1)}\delta_{lj} \quad \text{(33a)}$$

and because of the orthogonality conditions (35) the solutions of Eqs. (32a) and (33a) will be expressed in terms of the Lagrangian multipliers $\vartheta_{ij}^{(1)}$. Their elimination is achieved by the substitution into Eq. (35) and the use of their hermitean properties. The solution of the appropriate uncoupled equations provides the zeroth approximation for the iterative solution of Eq. (27) or can be used for the calculation of the second-order perturbed energy corresponding to a given uncoupled scheme.

Apparently, the numerical realization of the present perturbation approach requires more computational effort than in the case of the CHF scheme. Even the solution of the uncoupled orbital equations is much more complicated, since the operators $\mathscr{F}_i^{(0)}$ are not diagonal in the basis set utilized in the expansion (34). In principle one can use different basis sets for different perturbed orbitals, i.e., the basis sets which diagonalize a given $\mathscr{F}_i^{(0)}$ operator. However, this will lead to a rather cumbersome form of the orthogonality conditions.

The other point is concerned with the use of the hypervirtual orbitals. In principle we can employ any set of orbitals satisfying the appropriate orthogonality conditions. However, in order to maintain some of the mentioned bounding properties of the MC SCF perturbation theory they should be confined to the subspace which determines the MC SCF orbitals used in the construction of $\Psi^{(0)}$.

In comparison with the finite perturbation MC SCF approach [41–43] the analytical formulation offers the possibility of the study of several approximate techniques which are the counterparts of some successful uncoupled schemes devised for the one-configuration approximation. Also the numerical accuracy of the machine calculations does not have to be so high as in the finite perturbation approach [22]. Finally, the analytical form of the MC SCF perturbation theory has by definition proper asymptotic behaviour for the vanishing perturbation and will not lead to the splitting of the unperturbed state observed in the finite perturbation calculations [41].

The programming of the formulae derived in this paper is in progress and the corresponding *ab initio* results for the second-order atomic and molecular properties related to the external electric and/or magnetic field perturbations will be published in future. Thus far the only numerical illustration is available for the CNDO/2 [59] approximation of the present theory. In view of the crudeness of the CNDO/2 approximation we shall focus our attention on the comparison of several perturbation techniques.

5. A Comparison of the One- and Multiconfiguration SCF Perturbation Theories

In order to illustrate the fundamental differences between the one- and multiconfiguration approach let us consider the calculation of the electric dipole polarizability of the hydrogen molecule. In the all-valence-electron CNDO/2 approach the SCF and MC SCF wave functions will have the form [60]

$$\begin{aligned}\Psi^{(0)}_{\mathrm{SCF}} &= |g^{(0)}\bar{g}^{(0)}| \\ \Psi^{(0)}_{\mathrm{MC\ SCF}} &= a^{(0)}_{00}|g^{(0)}\bar{g}^{(0)}| + a^{(0)}_{12}|u^{(0)}\bar{u}^{(0)}| \end{aligned} \tag{38}$$

where

$$g^{(0)} = 2^{-1/2}(1s_a + 1s_b) \qquad u^{(0)} = 2^{-1/2}(1s_a - 1s_b)$$

Because of the valence-shell approximation the perpendicular component of the molecular polarizability as well as the polarizability of the hydrogen atom are both equal to zero. Thus, the calculations will refer only to the parallel component $\alpha_{\parallel}$. This can be identified with the polarizability anisotropy $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} = \alpha_{\parallel}$.

According to the expansion technique (34) the first-order perturbed orbitals are given by

$$g^{(1)} = c_{gu}u^{(0)} \qquad u^{(1)} = c_{ug}g^{(0)} = -c_{gu}u^{(0)}$$

and using the standard CNDO/2 approximations for the one- and two-electron integrals [59, 61] we obtain simple explicit expressions for $\alpha_{\parallel}$. The following perturbation methods have been considered

(1) the Dalgarno uncoupled SCF perturbation scheme [3, 14],

(2) the one-configuration CHF theory [4, 14, 62, 63],

(3) the Dalgarno-type uncoupled MC SCF perturbation scheme (Eq. (33a)),

(4) the coupled MC SCF perturbation method (Eq. (27), in the present case equivalent to Eq. (32a)),

and the corresponding numerical data are shown in Table 1.

Table 1. Results of the perturbation calculations of $\alpha_{\parallel}$ for the hydrogen molecule (in Å ^{3})

	Method			
R (a.u.)	Dalgarno UCHF	CHF	Uncoupled MC SCF	Coupled MC SCF
1.0	0.1267	0.2285	0.1333	0.2277
1.4	0.2886	0.4567	0.3157	0.4171
2.0	0.7654	0.9650	0.8816	0.6895
3.0	2.729	2.285	2.975	0.5733
4.0	7.348	4.130	6.109	0.1872
5.0	16.03	6.373	9.824	0.0427
6.0	29.76	8.951	14.21	0.0085
7.0	49.14	11.86	19.39	0.0015
8.0	74.76	15.13	25.29	0.0003
9.0	107.4	18.77	32.01	0.0000
10.0	147.8	22.79	39.51	0.0000
15.0	500.1	48.79	88.91	0.0000
20.0	1185.0	84.67	17.88	0.0000
25.0	2315.0	130.4	0.0011	0.0000
∞	∞	∞	0	0

According to the data of Table 1 for the equilibrium internuclear distance $R = 1.4$ a.u. the coupled MC SCF scheme leads to a lowering of the CHF value of $\alpha_{\parallel}$ [62, 63]. Thus, the MC SCF value of the polarizability anisotropy becomes closer to the experimental one (0.314 Å^3, [64]). Although this result seems to be meaningful, we are not going to attach any specific importance to the corresponding numerical value. Far more important consequences of using the MC SCF perturbation theory follow from the distance dependence of the computed polarizability anisotropy.

For physical reasons the polarizability anisotropy of the hydrogen molecule should vanish at large R. However, in the case of the one-configuration approach the CNDO/2 results behave asymptotically like R^3 and become infinite for a pair of separated hydrogen atoms. On the other hand, both the uncoupled and the coupled MC SCF result vanish for infinite R. Thus, since the one-configuration approach fails to predict the correct dissociation limit also the CHF (or UCHF) perturbation theory cannot account for proper asymptotic properties of the polarizability anisotropy. These shortcomings of the single determinant approximation are corrected when using the MC SCF perturbation theory. It is worth attention that the asymptotic behaviour of $\Delta\alpha$ does not depend on the semiempirical form of the perturbation approach and will also be valid in the *ab initio* calculations. This follows from the fact that all the relevant CNDO/2 approximations [59] are virtually correct for large internuclear separations.

For R close to the equilibrium bond distance the results of different methods are qualitatively similar. Thus, the CHF calculations should be confined either to molecules with a proper SCF dissociation limit or to the geometries close to the equilibrium configuration. However, it follows from the data of Table 1 that the polarizability derivatives with respect to R may be quite different even for the equilibrium configuration. This brings some doubts about the usefulness of the corresponding CHF calculations [65].

Finally, a few words should be added in connection with the so-called configuration interaction (CI) perturbation theories [66]. First of all in the ordinary CI approach based on the HF orbitals the convergence of the perturbation procedure will be rather slow. Some improvement can be gained in this respect by using the MC SCF $\Psi^{(0)}$ and the corresponding singly-excited configurations for $\Psi^{(1)}$. This form of the perturbation theory will be equivalent to the neglect of the terms of $\Psi^{(2)}$ bilinear in the first-order perturbed orbitals. Since these terms contributed to the second-order energy functional of the coupled MC SCF perturbation theory, the CI-type approaches cannot result in a complete optimization of the perturbed wave function. This resembles the features of the so-called single-excitation model [14, 15] in the one-configuration approximation. Moreover, the CI approach based on the MC SCF $\Psi^{(0)}$ can be considered as a natural extension of this model.

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