UNCOUPLED HARTREE-FOCK VARIATION-PERTURBATION METHODS AND THEIR APPLICATIONS. I. APPROXIMATIONS FOR THE FIRST-ORDER PERTURBED ORBITALS

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A new method for the approximation of the first-order perturbed orbitals in the Hartree-Fock perturbation theory is proposed. Combining both the expansion into a set of virtual orbitals and a generalized product-form approximation, the present method utilizes as far as possible the information embodied in all the available unperturbed functions.

An appropriate, simplified uncoupled Hartree-Fock variation-perturbation procedure is also considered and analysed. The proposed uncoupling scheme is examplified by a trial calculation of the electric dipole polarizability of the Be atom. The obtained numerical value (6.519 Å³) compares favourably with the results of more advanced perturbation treatments.

1. Introduction

The coupled Hartree-Fock (CHF) perturbation theory [1, 2] is currently considered as the best one-electron model for the calculation of the second- and higher-order atomic and molecular properties [3–7]. However, this theory suffers from several practical restrictions, and its application to really many-electron systems requires an enormous computational effort.

There are two fundamental difficulties in the practical use of the CHF method. The first impracticability arises from the existence of so-called coupling terms [8] in the CHF equations, while the second one is connected with the calculation of numerous two-electron integrals. Moreover, using the form of the CHF method proposed by Stevens, Pitzer and Lipscomb [3], one has to know an extensive set of virtual Hartree-Fock orbitals for the unperturbed system. Thus, the CHF scheme can hardly be applied to larger systems.

To make the CHF theory tractable in the case of large atoms and molecules several simplifications are introduced [3, 8]. The most important one is known as the uncoupling procedure [3, 8, 9]. The idea of this approximation lies in the partial [8] or complete [9]

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neglect of the selfconsistency terms which couple the CHF equations for the perturbed orbitals. Sometimes, the uncoupling procedure is additionally followed by an appropriate modification of the unperturbed Hartree-Fock potential [8, 10]. Furthermore, to avoid the use of virtual Hartree-Fock orbitals, the perturbed wave functions are determined by a direct application of the corresponding variation principles [8]. Amongst various possible forms of the trial perturbed orbitals their representation by the product of the unperturbed orbital and appropriate variation function seems to be especially useful and attractive. This so-called product-form approximation [8, 10–12] has been extensively utilized in the uncoupled Hartree-Fock (UCHF) variation-perturbation scheme developed by Karplus and Kolker [10].

The intrinsic restrictions of the Karplus-Kolker UCHF scheme have recently been analysed [13, 14]. It was shown, that within the product-form approximation for the perturbed orbitals, the validity of this simplified UCHF method can be reliably justified for pure imaginary perturbations [13], while for real perturbing operators an extension of the Karplus-Kolker approach is necessary. Thus, analysing the approximations involved in the Karplus-Kolker scheme [13, 15] we found unavoidable inclusion of some two-electron integrals which cancel each other in the case of pure imaginary perturbations but lead to additional terms in the Karplus-Kolker functional for real perturbing operators. Numerical results for the electric dipole polarizability of various atomic systems [14, 16] indicate that this improved UCHF scheme is superior to the original Karplus-Kolker approach. However, the calculated atomic dipole shielding factors are, similarly as in the Karplus-Kolker scheme [8, 17], far from the exact theoretical values. The observed differences, which are especially drastic for the Be- and Mg-series [16, 18, 19], were attributed to the partial invalidity of the anticipated product-form approximation of the first-order perturbed orbitals. It was already pointed out by Langhoff, Karplus and Hurst[8] that the product-form approximation does not shift the nodes of the unperturbed wave function and can lead to serious difficulties for some perturbing operators.

Quite similar difficulties arise also when the Karplus-Kolker UCHF scheme is employed for the calculation of the second-order energies related to molecular magnetic properties [10, 12]. The corresponding perturbations are expressed in terms of the angular momentum operator [5] and the first-order perturbed orbitals do not, in general, preserve the nodes of the unperturbed orbitals. This property can hardly be represented within the product-form approximation. To avoid these cumbersome features of this approximation Karplus and Kolker [12] considered a specific form of the perturbed orbitals but their approach has no chance for general application to other than linear molecules.

Apparently, the product-form approximation of the perturbed orbitals and simplicity of the Karplus-Kolker UCHF scheme are very attractive but in some cases appropriate extensions seem to be necessary. They should not, however, considerably increase the computational effort involved in the method. In this paper we shall discuss a more general form of the approximation for the first-order perturbed orbitals and also the resulting UCHF schemes. The form of the trial variation functions for the perturbed orbitals proposed in this paper involves the idea of the expansion into a set of virtual Hartree-Fock orbitals as well as an extended product-type approximation.

Obviously, a more general form of the perturbed orbitals requires a reconsideration of all the approximations leading to various UCHF approaches.

We do not consider here the CHF approach based on the proposed approximation of the perturbed orbitals. For the CHF scheme any specific approximation for the perturbed orbitals does not lead to a substantial reduction of the computational effort. We shall confine our discussion to several uncoupled Hartree-Fock perturbation schemes which, according to previous results [8, 16, 19, 20, 21], should give the perturbed energies comparable to those obtained in the CHF method.

2. The approximation of the perturbed orbitals

Suppose we know a complete set $\{u_1^0, u_2^0, ..., u_n^0, ..., u_m^0, ...\}$ of the Hartree-Fock orbitals of a given unperturbed closed-shell system with $2n$ electrons. Then, the first-order perturbed orbitals are exactly determined by the following expansion

$$u_i^1 = \sum_{p=n+1} c_{ip} u_p^0 \tag{1}$$

with the coefficients c_{ip} calculated from the CHF equations [3]. In practice, however, we have at our disposal only a finite, incomplete set of m $(m \geqslant n)$ unperturbed orbitals and we should like to approximate (1) as accurately as possible.

To introduce the proposed form of the perturbed orbitals we write down (1) as a sum of two components

$$u_i^1 = u_i^{1,a} + u_i^{1,b} \tag{2}$$

where

$$u_i^{1,a} = \sum_{p=n+1}^{m} c_{ip} u_p^0 \tag{3}$$

and $u_i^{1,b}$ denotes the remaining part of the exact expression. For this part we employ the idea of the product-form approximation [8, 10, 20]. In order to utilize the available unperturbed Hartree-Fock orbitals as far as possible, we shall define here what can be called the generalized product-form approximation:

$$u_i^{1,b} = Q_m \sum_{q=1}^{m} f_{iq} u_q^0 \tag{4}$$

where

$$Q_m = 1 - \sum_{p=1}^{m} |u_p^0\rangle \langle u_p^0| \tag{5}$$

projects out the subspace spanned by that set $\{u_1^0, u_2^0, ..., u_m^0\}$ involved in $u_i^{1,a}$. By f_{iq} we denote the appropriate variation functions, usually taken in the polynomial form with

linear variation coefficients[1]. In the case when $f_{iq} = $ const the usual form of the first--order perturbed orbitals [3] is obtained.

According to (3) and (4) the proposed approximation for the first-order perturbed orbital u_i^1 can be written as

$$u_i^1 = u_i^{1,a} + u_i^{1,b} = \sum_{p=n+1}^{m} c_{ip} u_p^0 + Q_m \sum_{q=1}^{m} f_{iq} u_q^0 \tag{6}$$

and has more flexible form than that adopted by Lipscomb *et al.* [3] or by Karplus and Kolker [10]. It is worth noting that its components $u_i^{1,a}$ and $u_i^{1,b}$ are defined in two mutually orthogonal subspaces of the corresponding Hilbert space. Assuming the ortho-normality of the unperturbed Hartree-Fock orbitals, the perturbed functions (6) satisfy automatically the necessary orthogonality conditions [3, 8]

$$\langle u_i^1 | u_j^0 \rangle + \langle u_i^0 | u_j^1 \rangle = 0 \quad i, j = 1, 2, ..., n. \tag{7}$$

Attention should also be paid to the special case of Eq. (6) when $m = n$. In this case the determination of the first-order perturbed orbitals does not involve the knowledge of the virtual Hartree-Fock orbitals which are rather rarely available in the literature. Thus, the generalized product-form approximation

$$u_i^1 = u_i^{1,b} = Q_n \sum_{q=1}^{n} f_{iq} u_q^0 \tag{8}$$

appears to be very promising from the practical point of view. Moreover, choosing an appropriate form of the variation functions f_{iq} one can completely avoid the node shift problems characteristic for the Karplus-Kolker scheme. In comparison with more general trial functions [23–25] some simplification of the resulting variation-perturbation UCHF equations should also be obtained owing to the explicit presence of the unperturbed orbitals in Eq. (8).

3. The uncoupling procedures and additional approximations

In what follows we shall keep as far as possible the notation used previously [13, 14]. For the one-electron perturbation the best first-order perturbed orbitals are determined by the extremization of the CHF functional [8]:

$$J_{\mathrm{CHF}}[u_i^1] = \langle u_i^1 | h^0 - e_i^0 | u_i^1 \rangle + \langle u_i^1 | h^1 - e_i^1 | u_i^0 \rangle + \langle u_i^0 | h^1 - e_i^1 | u_i^1 \rangle +$$

$$+ \sum_{j=1}^{n} (2 - \delta_{ij}) \left[\langle u_i^1 u_j^0 | G_{12} | u_i^0 u_j^1 \rangle + \langle u_i^1 u_j^1 | G_{12} | u_i^0 u_j^0 \rangle \right]. \tag{9}$$

It was shown [8, 14, 23, 24], however, that the non-diagonal $(i \neq j)$ coupling terms in Eq. (9) should not contribute significantly to the calculated second-order energy. Omitting

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[1] In general the approximation (4) can lead to linear dependencies in the basis set $(f_{iq} u_q^0)$ resulting in the instability of the corresponding variation solution. These eventual linear dependencies should be removed in the first step of the calculation by using an appropriate linear transformation [21, 22].

them we obtain the functional of the UCHF scheme known as the Method b' of Langhoff, Karplus and Hurst [8]:

$$J_{\text{UCHF,b}'}[u_i^1] = \langle u_i^1|h^0 - e_i^0|u_i^1\rangle + \langle u_i^1|h^1 - e_i^1|u_i^0\rangle +$$

$$+ \langle u_i^0|h^1 - e_i^1|u_i^1\rangle + \langle u_i^1 u_i^0|G_{12}|u_i^0 u_i^1\rangle + \langle u_i^1 u_i^1|G_{12}|u_i^0 u_i^0\rangle. \tag{10}$$

This functional corresponds to the most sophisticated uncoupling procedure and appears to be superior to the other UCHF schemes [8, 26], because it omits a spurious electron selfinteraction [26, 27].

To proceed further we shall consider this UCHF scheme as a background of our analysis. Substituting the trial function (6) into the functional (10) we obtain

$$J_{\text{UCHF,b}'}[u_i^1] = J_{\text{UCHF,b}'}[u_i^{1,a}] + J_{\text{UCHF,b}'}[u_i^{1,b}] + J_{ab} \tag{11}$$

i.e., the original functional separates into two independent functionals $J_{\text{UCHF,b}'}$ defined in two mutually orthogonal subspaces $\{u_i^{1,a}\}$ and $\{u_i^{1,b}\}$, and some cross terms included in J_{ab}

$$J_{ab} = \langle u_i^{1,a}|h^0 - e_i^0|u_i^{1,b}\rangle + \langle u_i^{1,b}|h^0 - e_i^0|u_i^{1,a}\rangle +$$

$$+ \langle u_i^{1,a} u_i^0|G_{12}|u_i^0 u_i^{1,b}\rangle + \langle u_i^{1,b} u_i^0|G_{12}|u_i^0 u_i^{1,a}\rangle +$$

$$+ \langle u_i^{1,a} u_i^{1,b}|G_{12}|u_i^0 u_i^0\rangle + \langle u_i^{1,b} u_i^{1,a}|G_{12}|u_i^0 u_i^0\rangle. \tag{12}$$

Taking into account the definitions (3) and (4) we can easily realize that the first two terms of (12) vanish identically. From the practical point of view it would be very useful to have a complete separation of the functional (11) into two independent parts. To achieve this we have to put all the two-electron integrals appearing in (12) equal to zero. This approximation has some numerical justification.

Recently we have proposed a new UCHF scheme based on the simple product-form approximation for the first-order perturbed orbitals and taking advantage of the complete neglect of all the non-Coulomb two-electron integrals [16]. The numerical perturbation-like analysis of this approach [14, 16] shows that the contribution of the Coulomb-type two-electron integrals is the only important contribution in the Method b' of Langhoff, Karplus and Hurst [8]. Assuming a more general validity of this result we can drop out the cross terms in (11). It can be easily shown that J_{ab} contains only two-electron integrals of non-Coulomb form, which according to the computational experience, are much smaller than the Coulomb ones. Evidently, a more complete numerical analysis of the proposed approximation is desired.

Neglecting the terms involved in J_{ab} we can separately analyse the contributions of $u_i^{1,a}$ and $u_i^{1,b}$ to the second-order energy. However, both the functionals appearing in

$$J_{\text{UCHF}}[u_i^1] = J_{\text{UCHF,b}'}[u_i^{1,a}] + J_{\text{UCHF,b}'}[u_i^{1,b}] \tag{13}$$

are still very complicated from the computational point of view — they contain numerous two-electron integrals and therefore, cannot provide a simple tool for the calculation

of the second-order atomic and molecular properties. Concerning the first part of Eq. (13) a simple but accurate procedure has recently been proposed by Caves and Karplus [26]. According to these authors we neglect in $J_{\text{UCHF},b'}[u_i^{1,a}]$ all the two-electron integrals which contain more than two different orbitals. Thus, a complete functional

$$J_{\text{UCHF},b'}[u_i^{1,a}] = \sum_{r=1+n}^{m} c_{ir}^* c_{ir}(e_r^0 - e_i^0) +$$

$$+ \sum_{r,s=n+1}^{m} [c_{ir}^* c_{is} \langle u_r^0 u_i^0 | G_{12} | u_i^0 u_s^0 \rangle + c_{ir}^* c_{is}^* \langle u_r^0 u_s^0 | G_{12} | u_i^0 u_i^0 \rangle] +$$

$$+ \sum_{r=n+1}^{m} [c_{ir}^* \langle u_r^0 | h^1 - e_i^1 | u_i^0 \rangle + c_{ir} \langle u_i^0 | h^1 - e_i^1 | u_r^0 \rangle] \tag{14}$$

is reduced to a simplified one

$$J_a[u_i^{1,a}] = \sum_{r=n+1}^{m} [c_{ir}^* c_{ir}(e_r^0 - e_i^0) + c_{ir}^* c_{ir} \langle u_r^0 u_i^0 | G_{12} | u_i^0 u_r^0 \rangle +$$

$$+ c_{ir}^* c_{ir}^* \langle u_r^0 u_r^0 | G_{12} | u_i^0 u_i^0 \rangle + c_{ir}^* \langle u_r^0 | h^1 - e_i^1 | u_i^0 \rangle +$$

$$+ c_{ir} \langle u_i^0 | h^1 - e_i^1 | u_r^0 \rangle]. \tag{15}$$

It should be mentioned that this reduction is only partly consistent with that involved in the approximation $J_{ab} = 0$. In (15) we keep some most important exchange-type integrals and there is no numerical evidence for their neglect. Probably their influence should not be very large and they could be omitted at the next step of approximation. The numerical results presented by Caves and Karplus indicate that this should even improve the results for pure-imaginary perturbations [26]. Nevertheless in what follows we shall keep this simplified UCHF functional in its form given by Eq. (15).

To consider the second part of the functional (13) we perform the appropriate substitutions and obtain

$$J_{\text{UCHF},b'}[u_i^{1,b}] = \sum_{r,s=1}^{m} \{ \langle u_{ir}^1 | h^0 - e_i^0 | u_{is}^1 \rangle -$$

$$- \sum_{k=1}^{m} \langle u_k^0 | u_{is}^1 \rangle \langle u_{ir}^1 | u_k^0 \rangle (e_k^0 - e_i^0) +$$

$$+ \langle u_{ir}^1 u_i^0 | G_{12} | u_i^0 u_{is}^1 \rangle + \langle u_{ir}^1 u_{is}^1 | G_{12} | u_i^0 u_i^0 \rangle -$$

$$- \sum_{k=1}^{m} [\langle u_{ir}^1 | u_k^0 \rangle \langle u_k^0 u_i^0 | G_{12} | u_i^0 u_{is}^1 \rangle + \langle u_k^0 | u_{is}^1 \rangle \langle u_{ir}^1 u_i^0 | G_{12} | u_i^0 u_k^0 \rangle +$$

$$+ \langle u_{ir}^1 | u_k^0 \rangle \langle u_k^0 u_{is}^1 | G_{12} | u_i^0 u_i^0 \rangle + \langle u_{is}^1 | u_k^0 \rangle \langle u_{ir}^1 u_k^0 | G_{12} | u_i^0 u_i^0 \rangle] +$$

$$+ \sum_{k,l=1}^{m} [\langle u_{ir}^1 u_k^0 \rangle \langle u_i^0 | u_{is}^1 \rangle \langle u_k^0 u_i^0 | G_{12} | u_i^0 u_l^0 \rangle +$$

$$+\langle u_{ir}^1|u_k^0\rangle\langle u_{is}^1|u_i^0\rangle\langle u_k^0 u_i^0|G_{12}|u_i^0 u_i^0\rangle]+$$

$$+\sum_{r=1}^m [\langle u_{ir}^1|h^1-e_i^1|u_i^0\rangle+\langle u_i^0|h^1-e_i^1|u_{ir}^1\rangle-$$

$$-\sum_{k=1}^m (\langle u_{ir}^1|u_k^0\rangle\langle u_k^0|h^1-e_i^1|u_i^0\rangle+\langle u_k^0|u_{ir}^1\rangle\langle u_i^0|h^1-e_i^1|u_k^0\rangle)]\} \qquad (16)$$

where

$$u_{ir}^1 = f_{ir}u_r^0. \qquad (17)$$

It is worth attention that almost all physically significant perturbations satisfy the condition

$$\langle u_{ii}^1|u_i^0\rangle = \langle f_{ii}u_i^0|u_i^0\rangle = 0 \qquad (18)$$

automatically due to symmetry. Thus in agreement with previous assumptions we can neglect all the two-electron integrals which follow from the orthogonality conditions. Such an approximation has been investigated for a simple product-form of the first-order perturbed orbitals and was shown to be a very good one [16]. It can be easily seen that the neglect of the two-electron non-orthogonality terms corresponds to the complete neglect of the non-Coulomb integrals, provided Eq. (18) is satisfied. To make the treatment consistent we have also to neglect[2] all the non-Coulomb two-electron integrals in $\langle u_{ir}^1 u_i^0|G_{12}|u_i^0 u_{is}^1\rangle$ and $\langle u_{ir}^1 u_{is}^1|G_{12}|u_i^0 u_i^0\rangle$.

Obviously, the same approximation should also be applied to the first term of the functional (16). According to the usual definition of the Hartree-Fock Hamiltonian h^0 [13] we obtain

$$\langle u_{ir}^1|h^0-e_i^0|u_{is}^1\rangle = \langle u_{ir}^1|u_{is}^1\rangle(e_s^0-e_i^0)+$$

$$+\tfrac{1}{2}\langle u_r^0|\nabla f_{ir}^*\cdot\nabla f_{is}|u_s^0\rangle+\tfrac{1}{2}(\langle f_{ir}\nabla u_r^0|\nabla f_{is}|u_s^0\rangle-$$

$$-\langle f_{ir}u_r^0|\nabla f_{is}|\nabla u_s^0\rangle)+$$

$$+\sum_{j=1}^n (\langle f_{ir}(1)u_r^0(1)f_{is}^*(1)u_j^0(2)|r_{12}^{-1}|u_j^0(1)u_s^0(2)\rangle-$$

$$-\langle f_{ir}(1)u_r^0(1)u_j^0(2)|r_{12}^{-1}|u_j^0(1)f_{is}(2)u_s^0(2)\rangle) \qquad (19)$$

where the two-electron part of (19) arises due to the non-local character of the Hartree-Fock potential [29]. Neglecting also in this part all the non-Coulomb-type two-electron

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[2] It should be mentioned that we treat the two-electron integral $\langle u_{ip}^1 u_j^0|r_{12}^{-1}|u_i^0 u_{jq}^1\rangle$ ($\langle u_{ip}^1 u_{jq}^1|r_{12}^{-1}|u_i^0 u_j^0\rangle$) as the Coulomb one, if $i = p$ and $j = q$ ($p = j$ and $q = i$), i.e., the corresponding integrals are classified with respect to the presence of the unperturbed orbitals. Because of the f_{ip} functions the present terminology is somewhat different from that commonly used [28].

integrals we finally obtain the simplified UCHF functional

$$J_b[u_i^{1,b}] = \sum_{r,s=1}^{m} [\langle u_{ir}^1|u_{is}^1\rangle (e_s^0 - e_i^0) +$$

$$+ \tfrac{1}{2}\langle u_r^0|\nabla f_{ir}^* \cdot \nabla f_{is}|u_s^0\rangle + \tfrac{1}{2}(\langle f_{ir}\nabla u_r^0|\nabla f_{is}, u_s^0\rangle -$$

$$- \langle f_{ir} u_r^0|\nabla f_{is}|\nabla u_s^0\rangle) - \sum_{k=1}^{m} \langle u_k^0|u_{is}^1\rangle \langle u_{ir}^1|u_k^0\rangle (e_k^0 - e_i^0)] +$$

$$+ \sum_{\substack{j=1 \\ j\neq i}}^{n} (\langle f_{ij}(1)u_j^0(1)f_{ij}^*(1)u_j^0(2)|r_{12}^{-1}|u_j^0(1)u_j^0(2)\rangle -$$

$$- \langle f_{ij}(1)u_j^0(1)u_j^0(2)|r_{12}^{-1}|u_j^0(1)f_{ij}(2)u_j^0(2)\rangle) +$$

$$+ \langle f_{ii}(1)u_i^0(1)f_{ii}^*(1)u_i(2)|r_{12}^{-1}|u_i^0(1)u_i^0(2)\rangle +$$

$$+ \langle f_{ii}(1)u_i^0(1)u_i^0(2)|r_{12}^{-1}|u_i^0(1)f_{ii}(2)u_i^0(2)\rangle -$$

$$- \langle f_{ii}(1)u_i^0(1)u_i^0(2)|r_{12}^{-1}|u_i^0(1)f_{ii}(1)u_i^0(2)\rangle +$$

$$+ \langle f_{ii}(1)u_i^0(1)f_{ii}(2)u_i^0(2)|r_{12}^{-1}|u_i^0(1)u_i^0(2)\rangle +$$

$$+ \sum_{r=1}^{m} [\langle u_{ir}^1|h^1 - e_i^1|u_i^0\rangle + \langle u_i^0|h^1 - e_i^1|u_{ir}^1\rangle -$$

$$- \sum_{k=1}^{m} (\langle u_{ir}^1|u_k^0\rangle \langle u_k^0|h^1 - e_i^1|u_i^0\rangle + \langle u_k^0|u_{ir}^1\rangle \langle u_i^0|h^1 - e_i^1|u_k^0\rangle)] \tag{20}$$

which approximates the functional $J_{\text{UCHF},b'}[u_i^{1,b}]$ of Eq. (13). Some properties of this functional will be discussed and analysed in the next Section.

4. Discussion and conclusions

The total approximate UCHF functional proposed in this paper

$$J[u_i^1] = J_a[u_i^{1,a}] + J_b[u_i^{1,b}] \tag{21}$$

separates into two independent parts J_a and J_b defined by Eq. (15) and Eq. (20), respectively. The properties of the functional J_a and some numerical examples of its application have been discussed by Caves and Karplus [26]. Due to the separation of J_a and J_b the same conclusions are also valid for the contribution of J_a to the total functional (21). Thus, we can confine our discussion only to this part of (21) which follows from the generalized product-form approximation for the first-order perturbed orbitals.

To simplify the notation we denote by J_1 all the one-electron integrals contributing to (20) and by J_2 this part of J_b which contains only two-electron integrals

$$J_b = J_1 + J_2. \tag{22}$$

It is worth attention that for a simple product-form approximation, $u_i^1 = f_{ii}u_i^0$ [10], J_1 becomes identical with the Karplus-Kolker functional. Within the same approximation

$J_1 + J_2$ is equivalent to the functional of the improved UCHF scheme proposed recently [13, 15, 16]. It was also shown [13, 15] that the final form of the corresponding functional depends on the character of the perturbing operator h^1. Therefore, one can also obtain some further simplification of the functional (20) by a separate analysis of real and pure imaginary perturbations. Apparently, the one-electron part J_1, which can be easily calculated, does not deserve particular attention and we shall consider only the two-electron terms appearing in J_b.

If h^1 is a real one-electron operator, then the following relation

$$f_{ij}^* = f_{ij}$$

is satisfied and J_2 is reduced to

$$J_2^r = \sum_{j \neq i}^n ([f_{ij}u_j^0 f_{ij}u_j^0 | u_j^0 u_j^0] - [f_{ij}u_j^0 u_j^0 | f_{ij}u_j^0 u_j^0]) + \\ + 2[f_{ii}u_i^0 u_i^0 | f_{ii}u_i^0 u_i^0] \qquad (23)$$

where

$$[a_1 a_2 ... | b_1 b_2 ...] = \int \int a_1(1) a_2(1) ... \frac{1}{r_{12}} b_1(2) b_2(2) ... dv_1 dv_2.$$

In the case of pure-imaginary perturbations we obtain

$$f_{ij}^* = -f_{ij}$$

and

$$J_2^{im} = \sum_{j \neq i}^n ([f_{ij}u_j^0 f_{ij}u_j^0 | u_j^0 u_j^0] - [f_{ij}u_j^0 u_j^0 | f_{ij}u_j^0 u_j^0]). \qquad (24)$$

It should be pointed out that in order to simplify the notation we assumed that all the unperturbed orbitals are real.

Comparing the functionals (23) and (24) with those previously derived [13, 16] it is worth noticing that the generalization of the product-type approximation for the first--order perturbed orbitals leads unavoidably to additional two-electron integrals. The numerical calculations indicate that the two-electron terms for $j \neq i$ entering (23) and (24) are not negligible. A complete neglect of these terms can only be justified within a simple product-form approximation for u_i^1 [13, 15]. Thus, the present simplified UCHF variation--perturbation procedure based on the functional (21) requires the calculation of some two-electron integrals. However, their number is much smaller than in the corresponding formulation of the Method b' of Langhoff, Karplus and Hurst [8]. On the other hand, in comparison with Karplus-Kolker scheme [10] the present approach makes the trial variation function more flexible and should be very fruitful when the node shift problems appear.

It should be also pointed out that the form (6) of the variation function utilizes as far as possible the information contained in the available unperturbed Hartree-Fock orbitals. The most important term of $u_i^{1,b}$, i.e., $f_{ii}u_i^0$ possesses all the nodes of the unperturbed orbital

u_0^i and this property should be reflected in good convergence of the method. Similar features of the product-form approximation has been noticed previously [8, 13, 16, 17, 30–32].

To get some information about the validity of our assumptions we have performed pilot calculations of the electric dipole polarizability of the Be atom. The unperturbed Hartree-Fock orbitals u_{1s}^0, u_{2s}^0 were taken from [33]. However, the excited orbitals have not been published in this source and we restricted our study to the generalized product-form approximation (4), i.e., to u_i^1 given by Eq. (3) with $m = n = 2$. For the electric field directed along z axis the first-order perturbed orbitals were expressed in the form

$$u_i^1 = u_i^{1,b} = f_{i,1s}u_{1s}^0 + f_{i,2s}u_{2s}^0 \quad (i = 1s, 2s) \tag{25}$$

with

$$f_{iq} = A_{iq,0}\frac{z}{r} + A_{iq,1}z \quad (q = 1s, 2s) \tag{26}$$

and $A_{iq,0}$, $A_{iq,1}$ being the variation parameters. Thus, four independent parameters have been used for each perturbed orbital. Because of linear dependencies in the basis set $\{f_{iq}u_q^0\}$ observed for f_{iq} with more than two terms, we did not attempt in the present paper to analyse the convergence of the method. The coresponding calculations with removed linearly dependent terms for more extensive representations of f_{iq} are in progress.

Extremizing the simplified functional (20) introduced in the present paper we obtained the electric dipole polarizability of Be atom equal to 6.519 Å³. Within the same approximation for the first-order perturbed orbitals the Method b′ [8] (functional (16)) gives 6.310 Å³, while the best result of this method is 6.736 Å³ [26]. Thus, the present simplified UCHF scheme leads to remarkably good agreement with the results of more complicated approaches. It is also worth noting that the best CHF values published in the literature are 6.758 Å³ [23] and 6.759 Å³ [34].

The present results should also be compared with those obtained within the simple product-form approximation for the first-order perturbed orbitals. In this case both the CHF scheme and the Method b′ lead to 6.26 Å³ [8]. The simplified variation-perturbation UCHF procedure proposed in [13] gives 6.24 Å³. Thus, it follows that the generalized product-form approximation removes the bounds imposed by the simple product-form of the first-order perturbed orbitals and provides a better representation of the effect of the external perturbing field.

A test of the accuracy of the first-order perturbed orbitals can be obtained by the evaluation of the dipole shielding factor [2, 8, 18]. However, the result for this quantity can hardly be expected to be successful within rather short representation (26) of the variation function. Nevertheless, the present result (2.26) is better than that obtained by using the Method b′ with simple product-form of the first-order perturbed orbitals (2.66 [8]). More extensive calculations of the electric dipole polarizability and dipole shielding factors for the Be atom and other atomic systems are in progress. The approach based on the functional (21) is also applied to the calculation of molecular magnetic properties. The results of all these calculations will be published separately.

Finally, it should be pointed out that the present scheme can also be considered from the point of view of Sinanoglu's ideas of Varied Portions Approach [35, 36]. According to [35] the validity of any simplified UCHF procedure can be justified if the terms neglected in the CHF functional do not contribute significantly to the corresponding second-order energy. Moreover, all these neglected terms can be accounted for by using an appropriate perturbation procedure. A similar technique has been used previously in the analysis of the Karplus-Kolker approximation [14] and provides a good estimate of the CHF result without solving the corresponding coupled equations.

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