

IMPROVED UNCOUPLED HARTREE-FOCK PERTURBATION THEORY

III. DIPOLE SHIELDING FACTORS

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The application of the previously proposed uncoupling scheme to the calculation of the mixed-type second-order properties is considered. The first-order perturbed Hartree-Fock orbitals obtained in the electric polarizability calculations are employed for the determination of the dipole shielding factors of 4- and 10-electron atoms and ions. A considerable improvement over the dipole shielding factors calculated by using the Karplus-Kolker first-order perturbed orbitals is obtained.

1. Introduction

Recently a new uncoupling scheme for the Hartree-Fock perturbation theory has been proposed [1, 2]. It was shown that this modified uncoupling scheme provides for a considerable improvement of the calculated second-order energy over that obtained in the uncoupled procedure due to Karplus and Kolker [3, 4]. Although this new uncoupled procedure involves the calculation of some two-electron integrals, it is much simpler than the other approaches based on similar assumptions [2, 4].

The numerical results for the electric dipole polarizability of 4- and 10-electron atoms and ions obtained by using this new uncoupled Hartree-Fock perturbation theory are in a fair agreement with the coupled approach results. These data indicate that the approximate first-order perturbed orbitals do adequately represent the perturbation of the outer electron shells in the atomic systems, being quite close to the first-order perturbed wave functions resulting from the coupled Hartree-Fock perturbation scheme. It was therefore of interest to investigate their applicability to the calculation of the mixed-type second-order properties. In this respect the atomic dipole shielding factors seem to provide for the best test of the calculated wave functions. Apparently, they can be evaluated by using the appropriate perturbation theory formula [5]. On the other hand, it can be shown that their accurate values are in fact independent on the form of the first-order perturbed orbitals, being

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equal to the ratio of the number of electrons and the nuclear charge [5]. It should be pointed out that the atomic dipole shielding factors are extremely sensitive to the accuracy of the first-order perturbed wave functions when calculated by means of the perturbation theory approach [4]. In comparison with the electric polarizabilities they also depend on the perturbation of inner electron shells. Even in the case of the coupled Hartree-Fock treatment with the product-form approximation for the perturbed orbitals, the calculated electric dipole shielding factors are considerably higher than the exact ones [4, 6].

2. The method of calculation

A description of the variation-perturbation procedure for the calculation of the first-order perturbed orbitals within the new uncoupled Hartree-Fock perturbation scheme has been given previously [1, 2]. The validity of the proposed treatment has also been widely discussed [4]. Thus, we can only summarize here some basic formulae which form the background of the considered uncoupled scheme.

The first-order perturbed orbitals u_i^1 are approximated in the so-called product form [2, 4]. Taking into account the orthogonality conditions, they can be written as

$$u_i^1 = x_i^1 - \sum_{k=1}^N \langle u_k^0 | x_i^1 \rangle u_k^0 \quad (1)$$

where

$$x_i^1 = f_i u_i^0 \quad (2)$$

u_i^0, u_k^0 are the unperturbed orbitals for the ground state and f_i is the correction to be determined variationally. The summation extends over all the doubly occupied orbitals of a given closed-shell system. According to Part II [2] a functional for the determination of the correction f_i within the modified uncoupled scheme is given by [2]

$$\begin{aligned} J[f_i] = & J_{KK}[f_i] + 2\langle u_i^0(1)f_i(1)u_i^0(2) | r_{12}^{-1} | u_i^0(1)u_i^0(2)f_i(2) \rangle - \\ & - 2 \sum_k^N \langle u_i^0 f_i | u_k^0 \rangle [3\langle u_k^0(1)u_i^0(2) | r_{12}^{-1} | u_i^0(1)u_i^0(2)f_i(2) \rangle - \\ & - \langle u_k^0(1)u_i^0(2) | r_{12}^{-1} | u_i^0(1)f_i(1)u_i^0(2) \rangle] + \\ & + \sum_k^N \sum_l^N \langle u_i^0 f_i | u_k^0 \rangle \langle u_i^0 f_i | u_l^0 \rangle [3\langle u_k^0 u_l^0 | r_{12}^{-1} | u_i^0 u_i^0 \rangle - \langle u_k^0 u_l^0 | r_{12}^{-1} | u_i^0 u_i^0 \rangle]. \end{aligned} \quad (3)$$

The one-electron perturbation h^1 has been assumed to be real. In the case of the static electric field perturbation (z -direction of the external electric field E is anticipated) the corresponding operator is given by

$$h^1 = -E_z z = -Ez. \quad (4)$$

In comparison with the functional of the Karplus-Kolker method [3] ($J_{KK}[f_i]$), the present treatment involves some two-electron integrals and partly accounts for the non-local character of the Hartree-Fock operator and the self-consistency requirements [2].

If the variation correction f_i is approximated by a polynomial expansion

$$f_i = -E \sum_{p=L_1}^{L_2} A_{ip} Z r^{p-1} \quad (5)$$

the extremization of the functional (3) leads to a set of inhomogeneous linear equations determining the unknown coefficients A_{ip} . Having obtained the corrections to all the atomic orbitals of a given atom or ion, one can easily calculate the corresponding electric dipole polarizability and electric dipole shielding factor

$$\beta_d = 2 \sum_i^N \left\langle u_i^i \left| \frac{z}{r^3} \right| u_i^0 \right\rangle \quad (6)$$

the substitution of Eq. (1) into Eq. (6) leads to the final formula

$$\beta_d = 2 \sum_i^N \left[\left\langle f_i u_i^0 \left| \frac{z}{r^3} \right| u_i^0 \right\rangle - \sum_k^N \langle u_k^0 | f_i u_i^0 \rangle \left\langle u_i^0 \left| \frac{z}{r^3} \right| u_k^0 \right\rangle \right] \quad (6a)$$

utilized in the present calculations.

3. Results and discussion

Two sets of calculations were performed. In the first set we used the previously calculated first-order perturbation corrections f_i [2] with $L_1 = 1$ and $L_2 = 2, 3, 4$ and 5 . The results obtained for some representatives of the beryllium- and neon-like systems are shown in Table I. A comparison with the results obtained in the coupled Hartree-Fock

TABLE I

The calculated dipole shielding factors for 4- and 10-electron atoms and ions. The orbital corrections f_i are given by Eq. (5) with $L_1 = 1$

Atom ¹ or ion	L_2^2			
	2	3	4	5
Be	2.420	2.562	2.637	2.658
B ⁺	2.008	2.119	2.158	2.147
C ⁺²	1.717	1.804	1.822	1.795
N ⁺³	1.499	1.570	1.575	1.541
F ⁻	1.013	1.091	1.199	1.217
Ne	1.023	1.053	1.081	1.090
Na ⁺	0.960	0.976	0.990	0.995
Mg ⁺²	0.890	0.901	0.909	0.914

¹ Except for F⁻, the unperturbed Hartree-Fock orbitals were taken from Ref. [10]. For F⁻ the corresponding source is Ref. [11].

² For explanation see Eq. (5) in the text.

TABLE II

A comparison of the calculated and exact dipole shielding factors of 4- and 10-electron atoms and ions

Atom or ion	Exact	Perturbed Hartree-Fock results					
		I ¹	II ¹	III ¹	IV ¹	This work	
						I ²	II ²
Be	1.0000	1.77	2.66	2.12	4.50	2.658	2.450
B ⁺	0.8000	1.60	2.15	1.78	3.15	2.147	1.948
C ⁺²	0.666 ₃	1.42	1.80	1.53	2.44	1.795	1.623
N ⁺³	0.5714	1.27	1.54	1.34	1.99	1.541	1.393
F ⁻	1.111 ₁	—	—	—	1.723	1.217	1.248
Ne	1.0000	—	—	—	1.478	1.090	1.114
Na ⁺	0.9091	—	—	—	1.313	0.995	1.014
Mg ⁺²	0.833 ₃	—	—	—	1.105	0.914	0.928

¹ Column headings correspond to: I — coupled Hartree-Fock perturbation theory, II — uncoupled Hartree-Fock perturbation scheme of Langhoff *et al.* [4], III — uncoupled Hartree-Fock perturbation scheme of Dalgarno [4], IV — uncoupled scheme of Karplus and Kolker [4]. The reference results were taken from Ref. [4] (Be-like systems) and from Ref. [6] (Ne-like systems) and correspond to the product form approximation of u_i^1 .

² Column I refers to five-term variation correction with $L1 = 1$ and $L2 = 5$. The results of column II were obtained with six-term variation correction ($L1 = 0$, $L2 = 5$).

calculations and the other uncoupled schemes, is given in Table II. Also the exact values of the corresponding dipole shielding factors are presented.

In comparison with the results of the uncoupled treatment due to Karplus-Kolker [4], the present method allows for a better representation of the mixed-type second-order properties to be achieved. The present results are comparable to those obtained within the uncoupled Hartree-Fock approach due to Langhoff, Karplus and Hurst [4] (so-called Method *b'*) and also to those calculated by using the uncoupled scheme of Dalgarno [4, 5]; the latter being somewhat better. In the case of Be-like systems there is, however, a striking discrepancy between the calculated and exact values of the dipole shielding factors. This discrepancy is extremely large in the case of the Karplus-Kolker uncoupled method. The present uncoupled Hartree-Fock perturbation scheme reduces the difference between the exact and approximate results but there is still considerable incongruity. On the other hand, the β_d values for the Ne-like systems are quite close to the exact ones.

It is worth noting that even in the frame of the coupled Hartree-Fock perturbation theory (with the product-type approximation for f_i), the calculated dipole shielding factors of the Be-series are considerably larger than the exact values. Unfortunately, there are no corresponding data for the Ne-like atoms and ions. Nevertheless, the source of the observed discrepancies can be sought in two directions.

First of all it can be supposed that the polynomial expansion (5), which begins with $L1 = 1$ is not suitable for the representation of the first-order perturbed orbitals with the accuracy required for the calculation of the dipole shielding factors. The form of the

perturbing potential

$$h^{0,1} = \frac{z}{r^3}$$

suggests an inclusion of the lower order term $\frac{z}{r}$. This correction should improve the first-order perturbed orbitals in the region where the perturbation becomes large.

To investigate the effect of the extension of the polynomial series by this additional term, we performed a second set of calculations with $L1 = 0$ and $L2 = 2, 3, 4$ and 5 . As it is shown by the data of Table III, some improvement of the calculated dipole shielding factors in beryllium-like systems is achieved. However, the dipole shielding factors for the Ne series become worse than those presented in Table I.

TABLE III

The calculated dipole shielding factors of 4- and 10-electron atoms and ions. The orbital corrections f_i are given by Eq. (5) with $L1 = 0$

Atom ¹ or ion	$L2^2$			
	2	3	4	5
Be	2.470	2.454	2.450	2.450
B ⁺	1.958	1.949	1.948	1.948
C ⁺²	1.629	1.623	1.623	1.623
N ⁺³	1.397	1.393	1.393	1.393
F ⁻	1.221	1.236	1.245	1.248
Ne	1.106	1.112	1.113	1.113
Na ⁺	1.010	1.013	1.014	1.014
Mg ⁺²	0.926	0.928	0.928	0.928

^{1,2} See Footnotes to Table I.

It should also be mentioned that the extension of the polynomial series (5) has practically no effect on the calculated electric dipole polarizability.

The explanation of this peculiar result obtained for the Ne-like systems can be sought in the formulation of the variation principle for the second-order energy $E^{2,0}$ connected with the electric field perturbation (4) $h^1 = h^{1,0}$. It should be pointed out that the mixed-type functional which determines the second-order energy $E^{1,1}$ and the dipole shielding factor gives neither minimum nor maximum [7, 8]. The approach adopted in the present paper is based on the assumption of the exactness of the first-order perturbed orbitals u_i^1 which justifies the use of Eq. (7) as providing the correct answer. Their apparent approximate character leads to a slow convergence or even an oscillatory character of the calculated dipole shielding factors.

Finally, some remarks should be made concerning a possible improvement of the dipole shielding factors for the Be-like atoms and ions. According to the data presented

in Table III, a further extension of the polynomial (5) should not result in the substantial reduction of the observed discrepancy between the exact and calculated values. The source of this disagreement should be sought elsewhere. It was pointed out by Langhoff *et al.* [4] that the product form approximation for u_i^1 rigidly preserves the nodes of the unperturbed orbital u_i^0 . Thus, this approximation precludes the flexibility of the first-order perturbed wave function in the regions close to the nucleus. This seems to be less important in the case of the Ne-series, since the principal contribution to the dipole shielding factor arises from $2p$ orbitals. On the other hand, $2s$ orbitals which are important in the Be-like systems have non-zero values at the nucleus and should be more sensitive to the accuracy of the product form approximation of the first-order perturbed orbitals. These conclusions are in agreement with the observed regularities. To obtain a further improvement of the electric dipole shielding factors some modification of the approximation (5) is needed. Obviously one can allow a more general variation treatment of the functional (3) to be performed at the cost of increasing the computational effort [12, 13], however the simplicity of the product-type approximation for u_i^1 seems to be attractive. It is believed that the expansion of the first-order perturbed orbitals into a more general series of the form

$$u_i^1 = \sum_j^N f_{ij} u_j^0$$

should improve the results for the mixed-type second-order properties without substantial increase of the computational complexity [9].

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