

Improved Uncoupled Hartree-Fock Perturbation Theory

V. Electric Dipole Polarizabilities of 12- and 18-Electron Atomic Systems

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The variation-perturbation uncoupled Hartree-Fock scheme is applied to the calculation of the electric dipole polarizabilities of Mg and Ar-like atomic systems. The results are compared with more elaborate coupled Hartree-Fock calculations and with experimental data and indicate the validity of the method.

Introduction

Recently a new approximate uncoupled Hartree-Fock (UCHF) variation-perturbation scheme^{1, 2} for the calculation of atomic and molecular second-order properties has been proposed. In the case of real perturbing operators this alternative simplified UCHF procedure has been shown to be superior to the DALGARNO scheme³ (Method c of LANGHOFF, KARPLUS and HURST⁴) and to the KARPLUS-KOLKER scheme⁵ (Method d of Ref. ⁴), and comparable in accuracy with the best UCHF scheme known as the Method b'^{4, 6}. For the electric dipole polarizability of 4- and 10-electron atomic systems a good agreement with coupled Hartree-Fock (CHF) results was found².

More recently, this improved UCHF scheme has been analysed⁷ using an appropriate perturbation-like technique⁸, and it was shown that some additional approximations in the corresponding functional are still possible without a loss of accuracy of the calculated properties. A neglect of some small two-electron integrals arising from the assumed orthogonality conditions^{2, 4, 7} resulted in what has been called the "reduced UCHF functional"⁷. The UCHF scheme based on this functional has been applied to the calculation of the electric dipole polarizability of Ne-like systems⁷ and has been found very successful.

The aim of the present paper is to provide some further examples of the usefulness of the proposed UCHF method for the calculation of the electric dipole polarizabilities. It should be pointed out that from the computational point of view the present method is much simpler than the CHF scheme, but that its validity is only approximately justified. Thus, a comparison with the corresponding more accurate

CHF results and with the experimental data for a sufficiently wide class of many-electron systems appears to be desirable.

The Method

A complete description of the method applied in the present study has been given previously^{2, 7}. Thus, for the sake of clarity of the presentation we only repeat some basic assumptions and formulae. The notation is the same as in previous papers of this series^{2, 7}.

The first-order perturbed orbitals u_i^1 are approximated in the product form^{4, 2}

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

and automatically satisfy the necessary orthogonality conditions⁴. The variation functions f_i are determined by the extremization of the following functional

$$\begin{aligned} J[f_i] = & \frac{1}{2} \langle u_i^0 | \nabla f_i \cdot \nabla f_i | u_i^0 \rangle + 2 \langle f_i u_i^0 | h^1 | u_i^0 \rangle \\ & - \sum_{k=1}^n [(e_k^0 - e_i^0) |\langle u_k^0 | f_i u_i^0 \rangle|^2 \\ & + 2 \langle u_k^0 | h^1 | u_i^0 \rangle \langle f_i u_i^0 | u_k^0 \rangle] \\ & + 2 \langle u_i^0(1) f_i(1) u_i^0(2) | r_{12}^{-1} | u_i^0(1) f_i(2) u_i^0(2) \rangle \end{aligned} \quad (2)$$

where both the perturbation operator h^1 and the variation correction f_i are assumed to be real. The derivation of the functional (2) and the corresponding approximations were discussed previously^{2, 7}. It should be pointed out that the "reduced UCHF functional" (2) differs from that of the Karplus-Kolker scheme^{4, 5, 9} by the presence of the two-electron integrals

$$2 \langle u_i^0(1) f_i(1) u_i^0(2) | r_{21}^{-1} | u_i^0(1) f_i(2) u_i^0(2) \rangle .$$



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This additional term is always positive and leads to the desired reduction of the Karplus-Kolker results for the electric dipole polarizabilities which, in turn, are considerably higher than the corresponding CHF values and also usually higher than the experimental data^{9, 10}.

Apparently, the choice of the product-form approximation (1) for the first-order perturbed orbitals has some disadvantages¹⁰⁻¹². However, this should not greatly affect the calculated dipole polarizabilities.

A suitable form of the variation problem is obtained in expanding the variation functions f_i into a set of known functions with linear variation coefficients⁵. Usually, the so-called polynomial expansion of f_i is accepted. In the case of the atomic dipole polarizabilities the functions f_i can be expressed in the form^{4, 11} (for z -direction of the electric field)

$$f_i = \sum_{p=L1}^{L2} A_{ip} z r^{p-1}. \quad (3)$$

This form of f_i has also been used in our previous calculations^{2, 7} and it was found that the convergence of the expansion (3) is sufficiently rapid. It was also found that the inclusion of the term z/r is of some importance^{7, 8, 12}.

Results and Discussion

In the present calculations of the electric dipole polarizability of atomic Mg and some Ar-like atomic systems the variation functions f_i were approximated in the form (3). The convergence of the method has been studied and, similarly as previously^{2, 7, 12}, was found to be very good. The final results, which are presented in Table 1, refer to the 6 term expansion of f_i with $L1=0$ and $L2=5$. Our results are com-

pared with available CHF calculations and with experimental data and also with the results of several approximate polarizability calculations by HARTMANN and KOHLMAIER¹³, THORHALLSSON et al.¹⁴, and PASCHALIS and WEISS¹⁵.

In order to indicate the superiority of the variation-perturbation scheme based on the functional (2) we also presented the corresponding results of the Karplus-Kolker method¹⁶. As shown by the data of Table 1 the present results are always lower than those obtained within the Karplus-Kolker scheme. This confirms our general conclusions^{2, 7} concerning the UCHF method based on the functional (2).

Although the reference CHF data are rather scarce, when available, they indicate that the present procedure can be considered as a good approximation of the CHF method. This latter is in turn considered as the best one-electron theory of the second-order properties¹⁷.

Comparing our results with the experimental data it must be mentioned that these latter are rather estimated than measured. A striking discrepancy between the present results and the corresponding experimental values is found for the Cl^- -ion. A similar disagreement has been also noticed previously for the F^- ion⁷ although, on the other hand, the UCHF calculations were in very good agreement with the CHF data. The CHF perturbation theory giving rather too small than too large electric dipole polarizabilities, we think that these discrepancies are due to inaccuracies of the experimental data. It should be pointed out that the correlation effects should rather increase the CHF values. A good example of the influence of the correlation effects is given by a comparison of various results for the H^- ion²⁵.

Table 1. Comparison of calculated and experimental electric dipole polarizabilities (in \AA^3).

Atom or ion	This work *	Calculated Reference results **			Experimental		
		CHF	HK	TFF	PW	YH	
Mg	11.766	12.04	—	14.1	—	19.4	7.0 ± 1.8^{10} , 7.4 ± 1.8^{19}
Cl^-	5.139	—	3.0	5.89	6.717	6.23	3.05^{20} , 2.97^{21}
Ar	1.763	1.570	1.8	1.99	—	2.32	1.642^{22}
K^+	0.885	—	0.94	0.944	1.323	1.08	0.80^{23} , 1.20^{21}
Ca^{++}	0.515	—	0.56	—	0.7684	0.620	0.54^{23} , 1.1^{21}

* These results were obtained with analytical SCF wavefunctions of CLEMENTI¹⁸.

** CHF = coupled Hartree-Fock results of KANEKO and ARAI²⁴, HK = variation calculations of HARTMANN and KOHLMAIER¹³, TFF = variation calculations of THORHALLSSON et al.¹⁴, PW = variation calculations of PASCHALIS and WEISS¹⁵, YH = results of the KARPLUS-KOLKER approach¹⁶.

A difference between the experimental and the theoretical results for the Mg atom appears also to be due to the inaccuracy of the experimental estimate¹⁹. This point of view is supported by a comparison with the corresponding CHF value which is higher than the experimental one but almost the same as that calculated using the functional (2). Although there is no rigorous proof that the CHF scheme gives a lower bound to the exact electric dipole polarizability, the correlation corrections²⁶ appear to be positive. Thus, an agreement of the present results with the CHF data seems to be more significant.

It is also shown by the data of Table 1 that the present variation-perturbation UCHF results are as a rule lower than those obtained using the approximate variation treatment of KIRKWOOD²⁷. The only exception is noticed for the HARTMANN and KOHL-

MAIER¹³ polarizability of the Cl^- ion which is lower than that found in this paper. In spite of the very crude character of the KIRKWOOD variation approach²⁷ the calculated electric dipole polarizabilities are unexpectedly good.

It follows from the comparisons presented in Table 1 that the UCHF variation-perturbation scheme based on the "reduced" functional (2) provides a good approximation of the CHF method. The present numerical results support our previous conclusions about the validity and usefulness of this simplified uncoupled Hartree-Fock perturbation approach. Finally, it should be mentioned that in the case of pure imaginary operators the approximations leading to the functional (2) give the functional of the Karplus-Kolker scheme^{1,2}. However, for real perturbing operators an inclusion of some two-electron integrals seems to be unavoidable.

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