Theoret. Chim. Acta (Berl.) 43, 161-164 (1976)

THEORETICA CHIMICA ACTA

Determination of Molecular Properties by the Method of Moments

VI. Application to Extended Hartree-Fock Wave Functions

Tamás Szondy

Computer Application Research and Development Center of the Chemical Industries, Budapest (Vegyipari Számitástechnikai Fejlesztési Társulás, Erzsébet kitályné útja 1/c, 1146 Budapest XIV, Hungary)

Ede Kapuy

Quantum Theory Group, Physics Institute, Technical University, Budapest (Kvantumelméleti Kutatócsoport, Müszaki Egyetem, Fizika Tanszék, Budafoki út 8, 1111 Budapest XI, Hungary)

Basic principles of a possibility of simplifying the unrestricted spin-projected Hartree-Fock equations by means of the method of moments are outlined.

Key words: Method of moments - Unrestricted spin-projected HF equations

1. Introduction

The application of the extended (unrestricted and spin-projected) Hartree-Fock method [1] to large molecular systems is hindered by difficulties resulting from the spin-projection. The aim of this paper is to outline the possibility of simplifying these problems by means of the method of moments. As in spite of the significant simplification some questions are open, (e.g. associated with the best algorithm for finding the best values of the variational parameters) our discussion will be confined to the basic principles.

2. The Simplification of the Extended Hartree-Fock Equations

Let H be the (electronic) Hamiltonian operator of a molecular system. We assume that H commutes with the square and the z-component of the total spin of the system. The extended Hartree-Fock wave function can be written as

$$U_{\mathrm{EHF}} = AP \prod_{I=1}^{N_\alpha} u(r_I, a_I)\alpha(s_I) \prod_{J=1}^{N_\beta} v(r_{N_\alpha+J}, b_J)\beta(s_{N_\alpha+J}). \tag{1}$$

Here A is the antisymmetrizer, P the operator projecting on to the required spin state, the u's and v's denote orbitals involving sets of variational parameters a_I and b_J, α and

β are the usual spin functions; N_α and N_β denote the number of electrons with α- and β-spin, respectively.

We start with observing that in most systems of practical interest the great majority of the electrons in the restricted Hartree-Fock approximation belong to double-occupied one-electron states. In order to avoid heavy notation we shall assume that all the electrons are such. This implies $N_\alpha = N_\beta = N$ and the system is in a singlet state.

In order to determine the values of the parameters a_I and b_J by the method of moments [2][1] a weight function generator W has to be chosen which involves at least as many variational parameters as U_{EHF}. Taking into account that presumably the majority of the parameters a_I and b_J are linear, a tempting form of the weight function generator is

$$W = W_{\mathrm{RHF}} = A \prod_{I=1}^{N} [c_{Ia} u(r_I, a_I) + c_{Ib} v(r_I, b_I)]\, \alpha(s_I) \times \prod_{J=1}^{N} [c_{Ja} u(r_{N+J}, a_J) + c_{Jb} v(r_{N+J}, b_J)]\, \beta(s_{N+J}), \qquad (2)$$

where the c's denote additional variational parameters. According to V, in the simplest formulatior of the method of moments (see Eq. (23) of V) the variational parameters can be determined from the requirement

$$\langle W_{\mathrm{RHF}} | H | U_{\mathrm{EHF}} \rangle / \langle W_{\mathrm{RHF}} | U_{\mathrm{EHF}} \rangle = E^M = \text{stationary}, \qquad (3)$$

(where stationary means minimum for the ground state) subject to the constraint

$$1 - [\langle W_{\mathrm{RHF}} | U_{\mathrm{EHF}} \rangle^2 / (\langle W_{\mathrm{RHF}} | W_{\mathrm{RHF}} \rangle \langle U_{\mathrm{EHF}} | U_{\mathrm{EHF}} \rangle)]^{1/2N} \ll 1, \qquad (4)$$

which qualitatively means $W_{\mathrm{RHF}} \approx U_{\mathrm{EHF}}$. This must be understood as follows: If (3) itself does not guarantee (4), the parameters in W_{RHF} must not be freely varied but subject to conditions ensuring (4). For further details and precautions we refer to V.

In any case it is necessary (and probably sufficient) to use (4) for the determination of the parameters c in W_{RHF}. If we require (without loss of generality) the pairing-theorem-like orthonormalization

$$\begin{aligned} &\langle u(r, a_I) | u(r, a_J) \rangle = \langle v(r, b_I) | v(r, b_J) \rangle = \delta_{IJ}, \\ &\langle u(r, a_I) | v(r, b_J) \rangle = \lambda_I \delta_{IJ} \qquad (I, J = 1, \ldots, N;\ 0 < \lambda_I < 1) \end{aligned} \qquad (5)$$

it can easily be verified that $[\ldots]$ in (4) is maximized by $c_{Ia} = c_{Ib}$ giving

$$[\ldots]^{1/2N} = \left(\prod_{I=1}^{N} (1 + \lambda_I)/2 \right)^{1/N},$$

i.e. the geometrical mean of the $(1 + \lambda_I)/2$'s.

Now, it follows from the theory of the restricted Hartree-Fock method that $PW_{\mathrm{RHF}} = W_{\mathrm{RHF}}$ and, of course, $AW_{\mathrm{RHF}} = W_{\mathrm{RHF}}$. This means that in the integrals entering (3) the annoying operators A and P in the definition of U_{EHF} can simply be disregarded: W_{RHF} is a single determinant and U_{EHF} becomes a single product.

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[1] The 5th paper of [2] will be referred to as V.

It must be emphasized that this procedure is not some hidden form of the unrestricted (but not spin-projected) Hartree-Fock method. The weight function generator W_{RHF} automatically acts as a projector.

The extension of these ideas to systems in a more complicated spin state is, in principle, straightforward. We must apply an "open-shell restricted Hartree-Fock" weight function generator and keep, if necessary, a drastically simplified spin projector acting only on the "open-shell" terms of the weight function generator.

3. Applications

The method outlined in the previous section has been tested by the ground state of the helium atom and the negative hydrogen ion. Wave functions

$$U_{\mathrm{EHF}} = AP \exp(-ar_1)\alpha(s_1) \exp(-br_2)\beta(s_2) \tag{6}$$

have been applied (disregarding A and P in (3)). Here a and b denote variational parameters; r_1 and r_2 are the distances of the electrons 1 and 2 from the fixed nucleus, respectively. The weight function generator then becomes

$$\begin{aligned} W_{\mathrm{RHF}} = A\,&[a^{3/2} \exp(-ar_1) + b^{3/2} \exp(-br_1)]\,\alpha(s_1) \\ &[a^{3/2} \exp(-ar_2) + b^{3/2} \exp(-br_2)]\,\beta(s_2). \end{aligned} \tag{7}$$

The results are listed in Table 1. They include the energies and wave functions calculated by the method of energy variation. The superscripts M and E refer to results obtained by the method of moments and the method of energy variation, respectively. The subscript RHF refers to the restricted Hartree-Fock results, i.e. $a = b$ in (6). The overlap integrals listed in Table 1 are

$$S_1 = \langle U^M_{\mathrm{EHF}} | U^E_{\mathrm{EHF}} \rangle / (\langle U^M_{\mathrm{EHF}} | U^M_{\mathrm{EHF}} \rangle \langle U^E_{\mathrm{EHF}} | U^E_{\mathrm{EHF}} \rangle)^{1/2}, \tag{8}$$

Table 1. Results of the calculations on the ground states of the helium atom and the negative hydrogen ion (atomic units). An explanation is given in the text

Helium Atom		
$E^M_{\mathrm{EHF}} = -2.87909$	$a = 1.080$	$b = 2.291$
$E^E_{\mathrm{EHF}} = -2.87566$	$a = 1.186$	$b = 2.186$
$E^E_{\mathrm{RHF}} = -2.84766$	$a = 1.687$	$b = 1.687$
$E_{\mathrm{EXACT}} = -2.90372$		
$S_1 = 0.99590$		
$S_2 = 0.93104$		
Negative Hydrogen Ion		
$E^M_{\mathrm{EHF}} = -0.51843$	$a = 0.207$	$b = 1.107$
$E^E_{\mathrm{EHF}} = -0.51327$	$a = 0.278$	$b = 1.045$
$E^E_{\mathrm{RHF}} = -0.47250$	$a = 0.687$	$b = 0.687$
$E_{\mathrm{EXACT}} = -0.52775$		
$S_1 = 0.96728$		
$S_2 = 0.69583$		

$$S_2 = \langle U^E_{\mathrm{RHF}} | U^E_{\mathrm{EHF}} \rangle / (\langle U^E_{\mathrm{RHF}} | U^E_{\mathrm{RHF}} \rangle \langle U^E_{\mathrm{EHF}} | U^E_{\mathrm{EHF}} \rangle)^{1/2}. \tag{9}$$

4. Discussion

The results presented in Table 1 indicate that the extended Hartree-Fock wave functions obtained by the method of moments may be reasonable approximations of those obtained by the method of energy variation. In general, it is probable that the method of moments will give stronger correlation effects in the wave function than the method of energy variation, as the weight function generator underestimates the correlation. In larger systems the effect of the other electrons is likely to hinder this "over-correlation". In any case it is probable that the method of moments can at least yield starting wave functions to a method-of-energy-variation treatment better than the restricted Hartree-Fock ones.

Acknowledgements. The authors are much indebted to Dr. M. Preisich and Prof. Dr. A. Kònya for continuous interest and support of their work.
Our best thanks are due to Mrs. Zs. Szabò for valuable discussions and other kinds of help.

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Received May 31, 1976