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Determination of Molecular Properties by the Method of Moments. II

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The wave functions and energies of a number of diatomic molecules have been determined for different nuclear separations by both the method of energy variation and the method of moments. The results obtained by the two methods are compared and indicate definite advantages of the method of moments over the method of energy variation.

Für eine Reihe zweiatomiger Moleküle werden für verschiedene Kernabstände die Wellenfunktionen und Energien nach der Methode der Energievariation und nach der neueren Momentenmethode bestimmt. Der Vergleich der Ergebnisse zeigt, daß die Momentenmethode erhebliche Vorteile besitzt gegenüber der üblichen Methode der Energievariation.

Les fonctions d'onde et les énergies de plusieurs molécules diatomiques ont été déterminées à différentes distances internucléaires par la méthode de variation de l'énergie et par la méthode des moments. Les résultats comparés des deux méthodes indiquent de nets avantages de la méthode des moments sur la méthode de variation de l'énergie.

1. Introduction

Some general problems concerning the use of the method moments for the calculation of molecular properties have been discussed in the first paper of this series[1]. The present paper gives the results of numerical calculations on diatomic molecules. The main aim of these calculations has been to compare the method of energy variation and the method of moments. The results support the conclusions of I concerning the advantages of the method of moments.

The notation of I will be used throughout the paper without further reference.

2. The Method

The calculations have been carried out on ground-state singlet systems in a one-determinant approximation. The method is a straightforward generalization of the Hartree-Fock-Roothaan method and consequently we shall only summarize the basic formulas without describing the details of their derivation. Our considerations will be limited to systems in the ground state.

Let $2N$ denote the number of electrons of the system, and let $p_i(\boldsymbol{r})$ and $q_i(\boldsymbol{r})$ $(i = 1, 2, \ldots, n)$ be two sets of basis functions depending on the position vector

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[1] The first paper of this series [1] will be referred to in the following as I.

$\boldsymbol{r}$ of an electron. Two sets of one-electron orbitals

$$s_i(\boldsymbol{r}) = \sum_{j=1}^{n} p_j(\boldsymbol{r})\,\alpha_{ji}\,, \tag{1}$$

$$t_i(\boldsymbol{r}) = \sum_{j=1}^{n} q_j(\boldsymbol{r})\,\beta_{ji} \tag{2}$$

are constructed from the basic sets and these are multiplied by the usual spin functions $a(\sigma)$ and $b(\sigma)$ to form the one electron spin orbitals $u_i(x)$ and $v_i(x)$ [2].

$$u_i(x) = s_i(\boldsymbol{r})\,a(\sigma)\,; \qquad u_{N+i}(x) = s_i(\boldsymbol{r})\,b(\sigma)\,; \tag{3}$$

$$\begin{gathered} v_i(x) = t_i(\boldsymbol{r})\,a(\sigma)\,; \qquad v_{N+i}(x) = t_i(\boldsymbol{r})\,b(\sigma)\,; \\ x = \{\boldsymbol{r}, \sigma\}\,. \end{gathered} \tag{4}$$

The variational wave function $\varphi_0(x, \alpha)$ and the 0'th weight function $w_0(x, \beta)$ are written in the form

$$\varphi_0(x, \alpha) = [(2N)!]^{-1/2}\,\mathrm{Det}\,(u_i(x_j)) \qquad (i, j = 1, 2, \ldots, 2N)\,, \tag{5}$$

$$w_0(x, \beta) = [(2N)!]^{1/2}\,v_1(x_1)\,v_2(x_2)\ldots v_{2N}(x_{2N})\,. \tag{6}$$

It will be assumed that the one-electron spin-orbitals are orthonormalized according to

$$\int \mathrm{d}\boldsymbol{r}\,t_i^*(\boldsymbol{r})\,s_j(\boldsymbol{r}) = \delta_{ij}\,. \tag{7}$$

In order to write down the energy expression and the equations for the determination of the variational parameters we need the following integrals and auxiliary quantities:

$$S_{ij} = \int \mathrm{d}\boldsymbol{r}\,q_i^*(\boldsymbol{r})\,p_j(\boldsymbol{r}) \qquad \text{(overlap integrals)}\,, \tag{8}$$

$$T_{ij} = -\tfrac{1}{2}\int \mathrm{d}\boldsymbol{r}\,q_i^*(\boldsymbol{r})\,\Delta p_j(\boldsymbol{r}) \qquad \text{(kinetic energy integrals)}\,, \tag{9}$$

$$V_{ij} = \int \mathrm{d}\boldsymbol{r}\,q_i^*(\boldsymbol{r})\,\mathscr{V}(\boldsymbol{r})\,p_j(\boldsymbol{r}) \qquad \text{(potential energy integrals)}\,, \tag{10}$$

$$C_{iklj} = \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}'\,q_i^*(\boldsymbol{r})\,q_k^*(\boldsymbol{r}')\,\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\,p_l(\boldsymbol{r}')\,p_j(\boldsymbol{r}) \qquad \text{(two electron integrals)}\,. \tag{11}$$

Here Δ denotes the Laplacian operator and $\mathscr{V}(\boldsymbol{r})$ the potential due to the nuclear charges and any external forces.

$$\Gamma_{lk} = 2\sum_{i=1}^{N} \alpha_{li}\beta_{ki}^* \qquad \text{(density matrix)}\,, \tag{12}$$

$$W_{kl} = \sum_{i=1}^{n}\sum_{j=1}^{n} \Gamma_{ji}(C_{iklj} - \tfrac{1}{2}C_{ikjl}) \qquad \text{(electron interaction energy integrals)}\,. \tag{13}$$

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[2] In order to avoid confusion with the variational parameters α_{ji} and β_{ji} we write $a(\sigma)$ and $b(\sigma)$ for the wave function describing "upward" and "downward" spin, respectively. σ denotes the spin variable.

The energy expression can now be written as

$$\mathscr{E}=\sum_{k=1}^{n}\sum_{l=1}^{n}\Gamma_{lk}(T_{kl}+V_{kl}+\tfrac{1}{2}W_{kl})\,. \tag{14}$$

The equations for the determination of the variational parameters can be derived from the requirements

$$\partial\mathscr{E}/\partial\beta_{ji}^{*}=0 \tag{15}$$

subject to the constraints (7). In the usual way we obtain the eigenvalue equation written in matrix notation as

$$(\boldsymbol{T}+\boldsymbol{V}+\boldsymbol{W})\,\boldsymbol{\alpha}=\boldsymbol{S}\boldsymbol{\alpha}\boldsymbol{E} \tag{16}$$

where $\boldsymbol{E}$ denotes the matrix of the Lagrangian multipliers of the constraints (7). Finally the constraints (7) give the matrix equation

$$\boldsymbol{\beta}^{+}\boldsymbol{S}\boldsymbol{\alpha}=\boldsymbol{I} \tag{17}$$

where $\boldsymbol{I}$ denotes the diagonal unit matrix.

3. The Results

The calculations have been carried out according to the following scheme:

For every molecule:

(a) A “starting basis set” $o_i(\boldsymbol{r})$ $(i=1,2,\ldots,n)$ has been chosen. The $o_i(\boldsymbol{r})$'s have been built up of Slater functions with fixed orbital exponents and fixed effective principal quantum numbers (chosen in most cases according to the Slater rules).

(b) Every function $o_i(\boldsymbol{r})$ has been expanded into a finite number of 1*s* Boys functions[3] (“lobe orbital approximation”) in different ways giving the functions

$$o_i^{(1)}(\boldsymbol{r}),\qquad o_i^{(2)}(\boldsymbol{r}),\,\ldots\,. \tag{18}$$

The details of the expansion are described in the tables and in the Appendix. The sets $o_i(\boldsymbol{r})$ are given in such an order that if they are chosen as basis sets in conventional Hartree-Fock-Roothaan calculations based on the method of energy variation then the sets with higher superscripts give better approximations to E_0. (In practice this means that the sets with higher superscripts are expanded into more Boys functions.)

(c) The basis sets $q_i(\boldsymbol{r})$ and $p_i(\boldsymbol{r})$ have been chosen in the form

$$q_i(\boldsymbol{r})=o_i^{(k)}(\boldsymbol{r})\,. \tag{19}$$

$$p_i(\boldsymbol{r})=o_i^{(l)}(\boldsymbol{r})\qquad (i=1,2,\ldots,n;\quad k\leqq l)\,. \tag{20}$$

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[3] Functions of the form

$$\exp(-\alpha r)\,r^{n+l}\,Y_{l,m}(\vartheta,\varphi)$$

will be referred to as Slater functions and functions of the form

$$\exp(-\alpha r^2)\,r^{2n+l}\,Y_{l,m}(\vartheta,\varphi)$$

as Boys functions.

Table 1

i	$o_i(\mathbf{r})$		Number of expanding Boys functions		
	Functional form	z-coordinate of the center	$o_i^{(1)}(\mathbf{r})$	$o_i^{(2)}(\mathbf{r})$	$o_i^{(3)}(\mathbf{r})$
H_2 molecule: Basis sets					
1	$N \times \exp(-1.00\, r)$	$+R/2$	1	2	4
2	$N \times \exp(-1.00\, r)$	$-R/2$	1	2	4
3	$N \times \exp(-2.00\, r)$	$+R/2$	1	2	4
4	$N \times \exp(-2.00\, r)$	$-R/2$	1	2	4
5	$N \times \exp(-1.00\, r)$	0	1	1	1
Li_2 molecule: Basis sets					
1	$N \times \exp(-2.70\, r)$	$+R/2$	1	2	4
2	$N \times \exp(-2.70\, r)$	$-R/2$	1	2	4
3	$N \times r \times \exp(-0.65 r)$	$+R/2$	2	4	5
4	$N \times r \times \exp(-0.65 r)$	$-R/2$	2	4	5
5	$N \times \exp(-1.00\, r)$	0	1	1	1
LiH molecule: Basis sets					
1	$N \times \exp(-2.70\, r)$	0	1	2	4
2	$N \times r \times \exp(-0.65 r)$	0	2	4	5
3	$N \times \exp(-1.00\, r)$	$+R$	1	2	4
4	$N \times \exp(-1.00\, r)$	$+R/2$	1	1	1
Be_2 molecule: Basis sets					
1	$N \times \exp(-3.70\, r)$	$+R/2$	1	2	4
2	$N \times \exp(-3.70\, r)$	$-R/2$	1	2	4
3	$N \times r \times \exp(-0.98 r)$	$+R/2$	2	4	5
4	$N \times r \times \exp(-0.98 r)$	$-R/2$	2	4	5
5	$N \times \exp(-1.00\, r)$	0	1	1	1
HF molecule: Basis sets					
1	$N \times \exp(-8.70\, r)$	0	1	4	
2	$N \times r \times \exp(-2.60\, r)$	0	2	4	
3	$N \times x \times \exp(-2.60\, r)$	0	2	4	
4	$N \times y \times \exp(-2.60\, r)$	0	2	4	
5	$N \times z \times \exp(-2.60\, r)$	0	2	4	
6	$N \times \exp(-1.00\, r)$	$+R$	1	4	
7	$N \times \exp(-1.00\, r)$	$+R/2$	1	1	

Table 2. *The choice of the basis functions $p_i(\mathbf{r})$ and $q_i(\mathbf{r})$ in the different calculations*

Molecule	1st approximation			2nd approximation		
	A	B	C	A	B	C
H_2, Li_2, LiH, Be_2	$k=1$	$k=1, l=2$	$l=2$	$k=1$	$k=1, l=3$	$l=3$
HF	$k=1$	$k=1, l=2$	$l=2$			

Table 3. *The equilibrium nuclear separations*

Molecule	1st approximation			2nd approximation		
	R_A	R_B	R_C	R_A	R_B	R_C
H_2	1.34	1.36	1.38	1.34	1.38	1.40
Li_2	<2	4.88	5.12	<2	5.16	5.32
LiH	2.12	2.76	2.86	2.12	2.76	2.86
Be_2	7.25	9.05	9.10	7.25	9.10	9.10
HF	1.78	1.72	1.70			

In the case $k=l$ the approximation is equivalent to determining the variational wave function by the method of energy variation, in the case $k<l$ the approximation is based on the method of moments.

(d) The calculations with the basis sets (19) and (20) have been carried out for every nuclear separation in the following three different approximations:

Approximation A:

$$q_i(\boldsymbol{r})=p_i(\boldsymbol{r})=o_i^{(k)}(\boldsymbol{r}) \tag{21}$$

("lower method-of-energy-variation approximation").

Approximation B:

$$q_i(\boldsymbol{r})=o_i^{(k)}(\boldsymbol{r}), \tag{22}$$

$$p_i(\boldsymbol{r})=o_i^{(l)}(\boldsymbol{r}) \quad (k<l) \tag{23}$$

("method-of-moments approximation").

Approximation C:

$$q_i(\boldsymbol{r})=p_i(\boldsymbol{r})=o_i^{(l)}(\boldsymbol{r}) \tag{24}$$

("higher method-of-energy-variation approximation").

(e) After having determined the wave functions $\varphi_0^A(x,\alpha)$, $\varphi_0^B(x,\alpha)$ and $\varphi_0^C(x,\alpha)$ belonging to the approximations A, B, and C the following quantities have been calculated.

The total ionization energies $E_A(R)$, $E_B(R)$ and $E_C(R)$.

The overlap integrals

$$S_{AB}(R)=\langle\varphi_0^A|\varphi_0^B\rangle,$$

$$S_{AC}(R)=\langle\varphi_0^A|\varphi_0^C\rangle,$$

$$S_{BC}(R)=\langle\varphi_0^B|\varphi_0^C\rangle.$$

The equilibrium nuclear separations R_A, R_B and R_C.

Here R denotes the nuclear separation.

The results obtained in this way are presented in the Tables 1–3 and the Figs. 1–5. All quantities are given in atomic unite. N symbolizes the normalization coefficient.

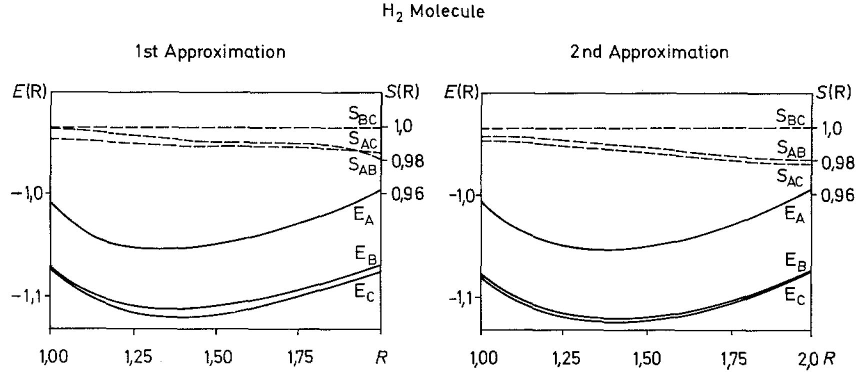

Fig. 1

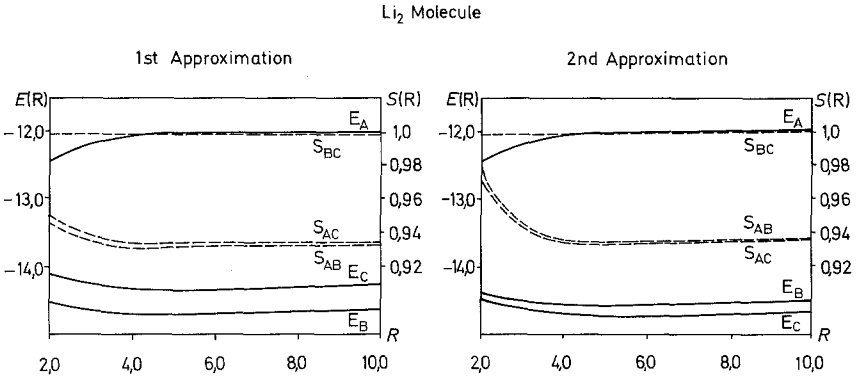

Fig. 2

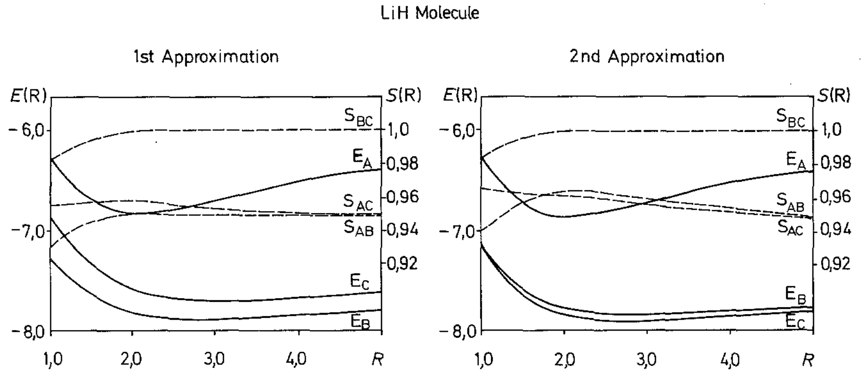

Fig. 3

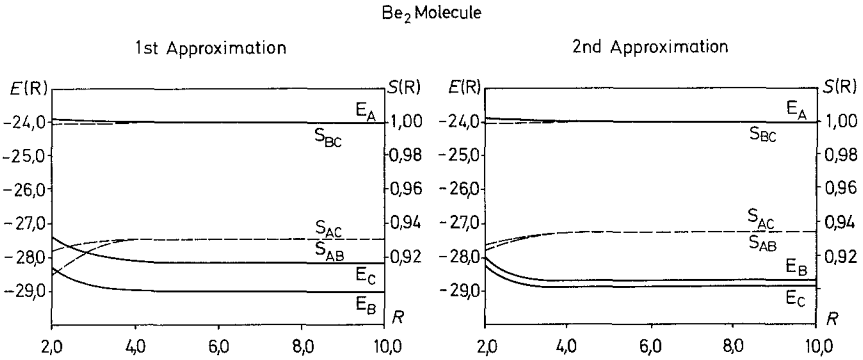

Fig. 4

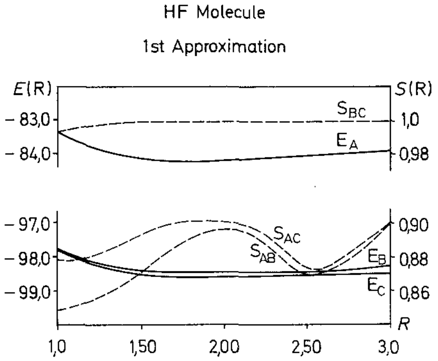

Fig. 5

4. Discussion

It can be seen from the results presented in Section 3 that the approximations *B* give a similar accuracy as the corresponding approximations *C* and that this accuracy is in most cases considerably higher than that obtained from the corresponding approximation *A*. We have thus to compare the computer times connected with the different approximations.

The main difference in the computer times result from the differences between the computer times needed for the calculation of the electron interaction integrals[4].

Although the estimates of computer time required for the calculation of the electron interaction integrals are more or less rough estimates, they are yet sufficiently reliable to draw the necessary conclusions.

If the total number of 1*s* Boys functions comprising the basis wave and basis weight functions (the $p_i(r)$'s and $q_i(r)$'s) is denoted by *m* and *n*, respectively, the computer time for the calculation of the electron interaction integrals is roughly proportional to the product m^2n^2. (In the case of the method of energy variation $m = n$.) The proportionality factor is, however, different for the method of moments and the method of energy variation. Namely in the case of the method of moments

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[4] It may be mentionned that except for the very lowest approximations an overwhelming part of the computer time has been spent in calculating the electron interaction integrals.

Table 4. *The approximate computer times required for the calculation of the electron interaction integrals. (In every calculation the time required for the calculation of the integrals in approximation A has been taken as unit)*

	1st approximation			2nd approximation		
	A	*B*	*C*	*A*	*B*	*C*
H_2	1	11	10	1	38	134
Li_2	1	11	12	1	25	43
LiH	1	11	10	1	26	62
Be_2	1	11	12	1	25	43
HF	1	12	14			

the only symmetry property of the integrals that can be utilized (apart from possible sterical symmetries of the molecule which have not been taken into account) is

$$C_{iklj} = C_{kijl} \tag{25}$$

while in the case of the method of energy variation the additional symmetry properties

$$C_{iklj} = C_{jkli}, \tag{26}$$

$$C_{iklj} = C_{ilkj} \tag{27}$$

can also be utilized. The computer times can thus roughly be estimated as

$$\text{const} \cdot n^4/8 \tag{28}$$

in the case of the method of energy variation and as

$$\text{const} \cdot m^2 n^2/2 \tag{29}$$

in the case of the method of moments. Because of the more complicated administration the constant factor is about 10–20 percent higher in the case of the method of energy variation than in the method of moments.

The results presented in the Table 4 indicate that a given degree of accuracy has been obtained by the method of moments always in practically equal or less time than by the method of energy variation.

Appendix

The Expansion of the Slater Functions

For a given Slater function the constants of the expansions have been determined in such a way that the integral

$$\int d\boldsymbol{r}[S(\boldsymbol{r}) - \sum_{i=1}^{n} c_i \exp(-b_i(\boldsymbol{r}-\boldsymbol{r}_i)^2)]^2 r^{-k}$$

should be minimum ($S(\boldsymbol{r})$ denotes the Slater function with orbital exponent 1, centered in the origin of the coordinate system). This procedure is equivalent to

Table 5

	1st	2nd	3rd	4th	5th	Overlap
$1s$ Slater function:						
c:	0.33833					
b:	0.37031					0.96689
c:	0.16596	0.28040				
b:	0.19119	1.40070				0.99712
c:	0.07418	0.21032	0.19904			
b:	0.12054	0.48204	3.14200			0.99978
c:	0.01498	0.10895	0.18597	0.17733		
b:	0.06747	0.19049	0.65178	3.65050		0.99995
$2s$ Slater function:						
c:	0.14507	−0.03560				
b:	0.11233	0.55026				0.99520
c:	0.05872	0.09694	−0.08836			
b:	0.06900	0.19560	1.70000			0.99985
c:	0.05227	0.12979	−0.04485	−0.09460		
b:	0.06580	0.19747	0.34959	3.65000		0.99994
c:	0.05662	0.11055	−0.00796	−0.02303	−0.09142	
b:	0.06810	0.19782	0.34973	0.49990	3.50000	0.99991
$3s$ Slater function:						
c:	0.08471	−0.08795				
b:	0.05601	0.95001				0.99922
c:	0.08024	0.03353	−0.10263			
b:	0.05543	0.19991	0.49998			0.99976
c:	0.07603	0.07231	−0.11952	−0.02985		
b:	0.05412	0.19992	0.34996	2.45000		0.99987
$4s$ Slater function:						
c:	0.10189	−0.09877				
b:	0.05000	0.16685				0.99714
c:	0.11739	−0.07492	−0.04497			
b:	0.05000	0.10000	0.34690			0.99873
c:	0.11782	−0.07691	0.02852	−0.07018		
b:	0.05000	0.10000	0.67610	0.43860		0.99877
$2p_z$ Slater function:						
c:	0.76714					
b:	0.16459					
z:	0.29804					0.97481
c:	0.49868	0.29387				
b:	0.11410	0.50850				
z:	0.30010	0.43790				0.99363
$3p_z$ Slater function:						
c:	0.65692					
b:	0.09199					
z:	0.29998					0.99823
c:	0.40817	0.08048				
b:	0.06552	0.19805				
z:	0.30000	1.35000				0.99905

maximizing the overlap between the Slater function and its expansion, the expansion being subject to the same normality constraint as the Slater function. Here $\boldsymbol{r}_i$ denotes the center of the i-th Boys function. $\boldsymbol{r}^{-k}$ is a weight factor. In case of s Slater functions k has been chosen 1 in order to improve the expansion in the regions important for the energy. The expansion of p Slater functions occurred with $k=0$.

All the constants c_i, b_i and $\boldsymbol{r}_i$ have been optimized.

The constants obtained in this way are tabulated (Table 5). Every table contains the expansions of a Slater function, that is the coefficients (c), the exponents (b) and in case of p_z Slater functions the z coordinate of the center $\boldsymbol{r}_i$ (the x and y coordinates are 0). For every Slater function several expansions are presented, differing from each other in the number of Boys functions. The overlap between the Slater function and its expansions is also given.

Some papers dealing with similar problems are listed in the reference.

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