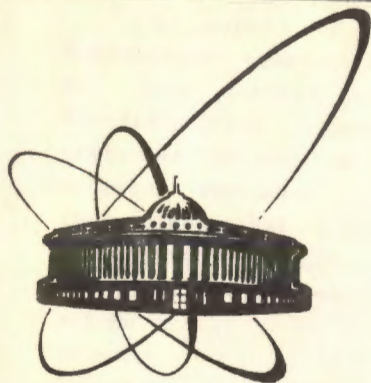


90-294



Объединенный
Институт
Ядерных
Исследований
Дубна

M52

E4-90-294

V.S.Melezhik

NEW METHOD
FOR SOLVING THREE-DIMENSIONAL
SCHROEDINGER EQUATION

Submitted to "Physics Letters A"

1990

1. INTRODUCTION

In paper /1/ the method for solving multidimensional Schroedinger equation for both the discrete and continuous spectra has been derived and its applications for a number of two-dimensional quantum mechanical problems have been presented. The subject of this paper is an application of the approach mentioned for solving Schroedinger equation in a three-dimensional infinite space. As an example, the helium-atom ground-state has been calculated. This is a classical problem of quantum mechanics and it is convenient for demonstration of the method efficiency since, on the one hand, this solution has been obtained with a high accuracy in the variational approach/2,3/, on the other hand, the solution of the problem by "direct" numerical methods (finite elements and finite differences) is yet a complicated problem which has all typical peculiarities and difficulties of genuine three-dimensional calculations and requires powerful computers for its solution (see, for example/4,5/).

2. SOLUTION TO A MULTIDIMENSIONAL SCHROEDINGER EQUATION

The essence of the method described in /1/ is the following. The partial-differential equation

$$\{ H(X) - E \} \cdot \Psi(X) = 0 \quad (1)$$

in the multidimensional space $X = \{R, \Omega\}$ is reduced to a system of differential-difference equations in terms of one of the variables R . For this purpose in the space X for the Hamiltonian of the system

$$H(X) = - \frac{1}{2 \cdot M} \frac{\partial^2}{\partial R^2} + U(R, \Omega) + f(R) \cdot h_0(\Omega) \quad (2)$$

(M is a reduced mass of the system)

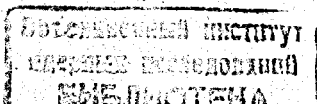
a subspace Ω is extracted

$$\{ h_0(\Omega) - \epsilon_n \} \cdot \varphi_n(\Omega) = 0 \quad (3)$$

with Hamiltonian $h_0(\Omega)$ and eigenfunctions $\varphi_n(\Omega)$ which satisfy the normalization conditions:

$$\int \varphi_n^*(\Omega) \cdot \varphi_n(\Omega) d\Omega = \delta_{nn} \quad (4)$$

In the subspace Ω the difference net $\Omega_i (i=1, 2, \dots, N)$ is



introduced and in its nodes the values of the wave function of the system are:

$$\Psi(R, \Omega) \rightarrow \Psi(r, \Omega_i) = \Psi_i(R). \quad (5)$$

Further, the discrete index $\beta (\beta=1, 2, \dots, \infty)$ is introduced corresponding to the set $\{n\}$ of quantum numbers which characterize the system (3) of basis functions. After that the set of eigenfunctions $\varphi_\beta(\Omega), \beta=1, 2, \dots, N$ of the Hamiltonian $h_0(\Omega)$ at nodal points Ω_i becomes the square matrix $\varphi_{i\beta} = \{\varphi_\beta(\Omega_i)\}$ of dimension $N \times N$. Assuming the system $\varphi_\beta(\Omega)$ to be a Chebyshev set on Ω /6/ we introduce the inverse matrix $\varphi_{\beta j}^{-1}$ and represent the searched wave function $\Psi(R, \Omega)$ as an expansion

$$\Psi(R, \Omega) = \sum_{j=1}^N \left(\sum_{\beta=1}^N \varphi_\beta(\Omega) \cdot \varphi_{\beta j}^{-1} \right) \cdot \Psi_j(R). \quad (6)$$

For this expansion the relation (5) is fulfilled automatically and following relations

$$(h_0(\Omega) \Psi(R, \Omega))_{\Omega=\Omega_i} = \sum_{j=1}^N \left(\sum_{\beta=1}^N \varepsilon_\beta \cdot \varphi_{i\beta} \cdot \varphi_{\beta j}^{-1} \right) \cdot \Psi_j(R) \quad (7)$$

$$(U(R, \Omega) \Psi(R, \Omega))_{\Omega=\Omega_i} = \sum_{j=1}^N U(R, \Omega_i) \left(\sum_{\beta=1}^N \varphi_{i\beta} \cdot \varphi_{\beta j}^{-1} \right) \cdot \Psi_j(R) = U(R, \Omega_i) \cdot \Psi_i(R) \quad (8)$$

are valid. Here we have assumed that the operator $U(R, \Omega)$ does not include the differentiation and integration over the variables Ω . Substituting expansion (6) into the Schroedinger equation (1) and using relations (7) and (8) we obtain the system of N differential-difference equations

$$\sum_{j=1}^N \left\{ \delta_{ij} \frac{d^2}{dR^2} + (2 \cdot M \cdot E - V_{ij}(R)) \right\} \cdot \Psi_j(R) = 0, \quad (9)$$

where

$$V_{ij}(R) = 2 \cdot M \cdot U(R, \Omega_i) \cdot \delta_{ij} + 2 \cdot M \cdot f(R) \cdot \sum_{\beta=1}^N \varepsilon_\beta \cdot \varphi_{i\beta} \cdot \varphi_{\beta j}^{-1}.$$

The idea to introduce "discrete variables" Ω_i for internal coordinates Ω was considered earlier (see, for example Ref. /7-9/ and refs. therein). The approach expounded here is more close to the "discrete variable representation" /7/. In paper /1/ it has been

demonstrated how to obtain the latter in this approach.

Following papers /1, 10/, we formulate the eigenvalue problem for the system of equations (9) as a nonlinear equation $F(z) = 0$ for unknown eigenvalue E and eigenfunction $\Psi_i(R), z = \{E, \Psi_i(R)\}$:

$$\begin{aligned} F_1(z) &\equiv \sum_{j=1}^N \left\{ \delta_{ij} \frac{d^2}{dR^2} + (2 \cdot M \cdot E \cdot \delta_{ij} - V_{ij}(R)) \right\} \cdot \Psi_j(R) = 0 \\ F_2(z) &\equiv \Psi_i(0) = 0 \\ F_3(z) &\equiv \Psi_i(R_m) = 0 \\ F_4(z) &\equiv \sum_{ij} g_{ij} \int_0^{R_m} \Psi_i(R) \cdot \Psi_j(R) \cdot dR - 1 = 0, \end{aligned} \quad (10)$$

where boundary conditions at $R=0$ and $R=R_m \rightarrow \infty$ and a normalization condition for the searched wave function are taken into account (here $g_{ij} = \sum_{\beta} (\varphi_{\beta i})^{-1} \cdot \varphi_{\beta j}$).

The solution z^* of the problem (10) has been derived in the approach /10, 11/ based on a continuous analog of the Newton method /12/. It is easy to see that the eigenfunction of the multidimensional Schroedinger equation (1) constructed from $\Psi_i^*(R)$ by formula (6) satisfies the same boundary conditions as $\varphi_\beta(\Omega)$ at the boundary of the volume Ω and possess the same symmetry.

3. DIFFERENTIAL-DIFFERENCE EQUATION FOR A HELIUM ATOM

The Schroedinger equation (1) for a helium-atom S-state in hyperspherical coordinates /13/

$$R^2 = r_1^2 + r_2^2 \in [0, \infty); \quad \alpha = \text{atan}(r_1 / r_2) \in [0, \pi] \quad (11)$$

$$\cos \theta = (r_1 \cdot r_2) / (r_1 \cdot r_2),$$

where r_1 and r_2 are distances between electrons and a nucleus, and the volume element is defined as $dr = R^5 \cdot dR \cdot \sin^2 \alpha \cdot d\alpha \cdot \sin \theta \cdot d\theta$, has the form

$$\left\{ \frac{1}{R^5} \frac{\partial}{\partial R} R \frac{\partial}{\partial R} + \frac{4}{R^2} \cdot \square^* + 2 \cdot (E - U(R, \alpha, \theta)) \right\} \cdot \Psi(R, \alpha, \theta) = 0, \quad (12)$$

where

$$\Delta^* = \frac{1}{\sin^2 \alpha} \left(\frac{\partial}{\partial \alpha} \sin^2 \alpha \frac{\partial}{\partial \alpha} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right)$$

$$U(R, \alpha, \theta) = \frac{1}{R} \left(-\frac{2}{\sin(\alpha/2)} - \frac{2}{\cos(\alpha/2)} + 1/\sqrt{1 - \sin \alpha \cdot \cos \theta} \right)$$

Taking the searched wave function as $\Psi(R, \alpha, \theta) = R^{-5/2} \sin^{-1} \alpha \cdot \psi(R, \alpha, \theta)$, we transform equation (12) to a form convenient for the reduction to the system of differential-difference equations (9):

$$\left\{ \frac{\partial^2}{\partial R^2} - h_0(\alpha, \theta) \cdot R^{-2} + 2 \cdot (E - U(R, \alpha, \theta)) \right\} \cdot \psi(R, \alpha, \theta) = 0, \quad (13)$$

$$\text{where } h_0(\alpha, \theta) = -4 \left(\frac{\partial^2}{\partial \alpha^2} + \frac{1}{\sin^2 \alpha} \frac{\partial}{\partial \alpha} \sin \theta \frac{\partial}{\partial \theta} \right)$$

$$U(R, \alpha, \theta) = \left(-2/\sin(\alpha/2) - 2/\cos(\alpha/2) + 1/\sqrt{1 - \cos \theta \cdot \sin \alpha} \right) \cdot R^{-1} - 1/8 \cdot R^{-2}$$

and the volume element is equal to $d\tau = dR \cdot d\alpha \cdot \sin \theta \cdot d\theta$.

Here it is convenient to take the subspace Ω as the rectangle $\Omega = \{\alpha, \theta\}$, where $\alpha \in [0, \pi/2]$ and $\theta \in [0, \pi]$ and basis functions $\varphi_\beta(\Omega)$ as

$$\varphi_\beta(\Omega) = \sin m\alpha \cdot P_l(\theta) \quad (14)$$

here $\beta = \{m, l\} = 1, 2, \dots, N$, where $l = n_\theta - 1$, $n_\theta = 1, 2, \dots, N_\theta$

$$\text{and } m = \begin{cases} 2 \cdot n_\alpha - 1, & \text{for singlet states} \\ 2 \cdot n_\beta, & \text{for triplet states} \end{cases}; \quad n_\alpha = 1, 2, \dots, N_\alpha, \quad N = N_\alpha \cdot N_\theta.$$

In this case the singularity $\sin^{-2} \alpha$ in the operator $h_0(\Omega)$

$$h_0(\Omega) \cdot \varphi_\beta(\Omega) = 4 \cdot \left(m^2 + \frac{1 \cdot (1+1)}{\sin^2 \alpha} \right) \cdot \varphi_\beta(\Omega) \quad (15)$$

as $\alpha \rightarrow 0$ is removed. Substituting the expansion (6) with basis functions (14) into equation (13) we obtain the system of

*) Wave functions of the helium atom are characterised by a certain symmetry with respect to the exchange $\alpha \rightarrow \pi - \alpha$: $\psi(R, \alpha, \theta) = \psi(R, \pi - \alpha, \theta)$ for singlet and $\psi(R, \alpha, \theta) = -\psi(R, \pi - \alpha, \theta)$ for triplet states.

differential-difference equation for a helium-atom S-state:

$$\sum_{j=1}^N \{ \delta_{ij} \frac{d^2}{dR^2} + (2 \cdot M \cdot E \cdot \delta_{ij} - V_{ij}(R)) \} \cdot \psi(R) = 0, \quad (16)$$

where

$$V_{ij}(R) = 4 \cdot \left\{ \sum_{\beta=\{m, l\}}^N (m^2 + \frac{1 \cdot (1+1)}{\sin^2 \alpha_i}) \cdot \sin m\alpha_i P_l(x_i) \cdot \varphi_{\beta j} \right\} \cdot R^{-2} + \delta_{ij} \cdot \left\{ 2 \cdot (-2/\sin(\alpha_i/2) - 2/\cos(\alpha_i/2) + 1/\sqrt{1 - x_i \cdot \sin \alpha_i}) \cdot R^{-1} - 1/4 \cdot R^{-2} \right\}$$

$$\beta = \{m, l\} = 1, 2, \dots, N; \quad m = \begin{cases} 2 \cdot n_\alpha - 1 & \text{for singlet} \\ 2 \cdot n_\alpha & \text{for triplet} \end{cases}; \quad n_\alpha = 1, 2, \dots, N_\alpha;$$

$$l = n_\theta - 1; \quad n_\theta = 1, 2, \dots, N_\theta;$$

$$i = \{i_\alpha, i_\theta\}; \quad i_\alpha = 1, 2, \dots, N_\alpha; \quad i_\theta = 1, 2, \dots, N_\theta; \quad N = N_\alpha \cdot N_\theta$$

$$x_i = \cos \theta_{i_\theta} \in [-1, 1].$$

4. BOUND STATES OF A HELIUM ATOM

The functional equation (10) has been solved by the algorithm /10/ with finite-difference approximation order $o(h_R^2)$ of the system (9) /11/. Newton iterations $z_k \rightarrow z^*$ converge from the initial approximation

$$z_0 = \{ E = -4.0, \psi_i(R) = 4.0 \cdot R^2 \cdot \sin \alpha \cdot \exp[-1.69 \cdot R \cdot (\sin(\alpha/2) + \cos(\alpha/2))] \}$$

to the value $\delta_k = \max |F_i(z_k)| \leq 10^{-6}$ at $k=5-6$ iterations. Calculations of the helium-atom ground-state (singlet) have been performed at $h_R = 0.05$, $R_m = 8$ and $F_2(z) = \psi_i(R=0)$. Here we do not examine the dependence of the solution E^* on the step h_R and the limit R_m of integration, and on the approximation $F_2(z) = 0$ of the wave function asymptotics $\psi(R, \Omega)$ as $R \rightarrow 0$ /13/ since this question has been studied /11/ and the procedure to make $E(h_R, R_m)$ more precise as $h_R \rightarrow 0$ is a well elaborated problem of computational mathematics (see, for example /6, 14/). As follows from numerical estimations, the total error ΔE due to the finite step of integration h_R and the approximation $\psi(R=0) = 0$ of wave functions asymptotics at point $R=0$ equals $|\Delta E| \leq 10^{-3}$ in our case. The error due to an approximation $F_3(z) = \psi_i(R_m) = 0$ of the boundary condition $\psi(R_m, \Omega) = 0$ is negligible as compared with ΔE .

Let us test the dependence of a solution $E(N_\alpha, N_\theta)$ on the step of the difference net Ω_i . It is natural to take roots of Legendre polynomial $P_{N_\theta+1}(x)$ (i.e. nodes of the Gauss quadrature formula of an order $N_\theta+1$) as coordinates x_i of grid points Ω_i . As coordinates α_i , roots of polynomials:

$$\sin[(2 \cdot N_\alpha + 1) \cdot \alpha] \quad (u), \quad \cos(2 \cdot N_\alpha \cdot \alpha) \quad (l) \quad \text{and} \quad \sin[2 \cdot (N_\alpha + 1) \cdot \alpha] \quad (11)$$

have been used. In this cases it is possible to simplify the calculation of coefficients g_{ij} of $F_4(z)$ using as g_{ij} weights of Gauss quadrature formulas. In the second and third lines of Table 1 results for $E(N_\alpha, N_\theta)$ as functions of N_α and N_θ for above-mentioned cases (u) $\bar{E}^{(0)}$ and (l) $\underline{E}^{(0)}$ are presented. It follows from numerical estimations that these quantities $\bar{E}^{(0)}$ and $\underline{E}^{(0)}$ for $4 \leq N_\alpha, N_\theta \leq 6$ can be represented as:

$$\bar{E}^{(0)}(N_\alpha, N_\theta) = E^* + 0.92 \cdot N_\alpha^{-1} - 0.18 \cdot N_\theta^{-2} \quad (17.u)$$

$$\underline{E}^{(0)}(N_\alpha, N_\theta) = E^* - 0.58 \cdot N_\alpha^{-1} - 0.16 \cdot N_\theta^{-2} \quad (17.l)$$

with the accuracy of an order $\approx \Delta E$. Since the dependence of quantities $\bar{E}^{(0)}$ and $\underline{E}^{(0)}$ in the leading order of N_α and N_θ in the decompositions (17) is the same, this makes possible the solution to be more precise

$$\bar{E}^{(s)}, \underline{E}^{(s)} = 1/2 \cdot (\bar{E}^{(s-1)} + \underline{E}^{(s-1)}), \quad (18)$$

The convergence of the iteration procedure (17) is demonstrated in Table 1 and Figure. The process has been cut as a "corridor" $\Delta_s = |\bar{E}^{(s)}(N_\alpha=N_\theta=6) - \underline{E}^{(s)}(N_\alpha=N_\theta=6)|$ achieved at $2 \cdot |\Delta E| \leq 2 \cdot 10^{-3}$.

The middle of the "corridor" $E = -2.9034$ is close to results obtained by the "direct" numerical methods of finite elements $E = -2.9032/4$, and finite differences $E = -2.9036/5$. A more accurate value, obtained in the variational approach, is $E = -2.90372/2,3$. As is known, the variational and finite-difference approaches provide only upper approximations to a ground-state energy of the system. The same result has been obtained in the above-mentioned finite-differences calculation/5/.

Taking the difference net α_i as roots of the polynomial (11) we

Table 1

The convergence of the iteration procedure (18):
 $\bar{E}^{(s)}, \underline{E}^{(s)} = 1/2 \cdot (\bar{E}^{(s-1)} + \underline{E}^{(s-1)})$

$N_\alpha \cdot N_\theta$	2·2	3·3	4·4	5·5	6·6
$\bar{E}^{(0)}$	-2.539911	-2.668384	-2.738412	-2.780601	-2.809085
$\underline{E}^{(0)}$	-3.154215	-3.078660	-3.029299	-2.996641	-2.974488
$\bar{E}^{(1)}$	-2.847063	-2.873522	-2.883856	-2.888621	-2.891787
$\underline{E}^{(1)}$	-3.154215	-3.078660	-3.029299	-2.996641	-2.974488
$\bar{E}^{(2)}$	-2.847063	-2.873522	-2.883856	-2.888621	-2.891787
$\underline{E}^{(2)}$	-3.000639	-2.976091	-2.956577	-2.942631	-2.933138
$\bar{E}^{(4)}$	-2.885457	-2.899165	-2.902037	-2.902123	-2.902125
$\underline{E}^{(4)}$	-2.923851	-2.924807	-2.920217	-2.915626	-2.912463
$\bar{E}^{(6)}$		-2.899165	-2.902037	-2.902123	-2.902125
$\underline{E}^{(6)}$		-2.905655	-2.906582	-2.905499	-2.904710

may accelerate the convergence of the method essentially (see Table 2):

$$\bar{E}^{(0)}(N_\alpha, N_\theta) = E^* - E_\theta \cdot N_\theta^{-2} - E_\alpha \cdot N_\alpha^{-\gamma}, \quad (19)$$

where $E_\alpha, E_\theta > 0$ and $\gamma \geq 4$ as $N_\alpha \geq 5$.

But in this case we could not find the appropriate difference net Ω_i for obtaining the expansion "corresponding" to (19) and construct an iteration procedure analogous to (18).

All calculations have been performed at the CDC-6500 computer whose central memory (less than 1 Mbt) strongly limited the number $N = N_\alpha \cdot N_\theta \leq 40$ of equations of the system to be solved/11/. The calculation of Z^* (i.e. binding energy and correspondent wave

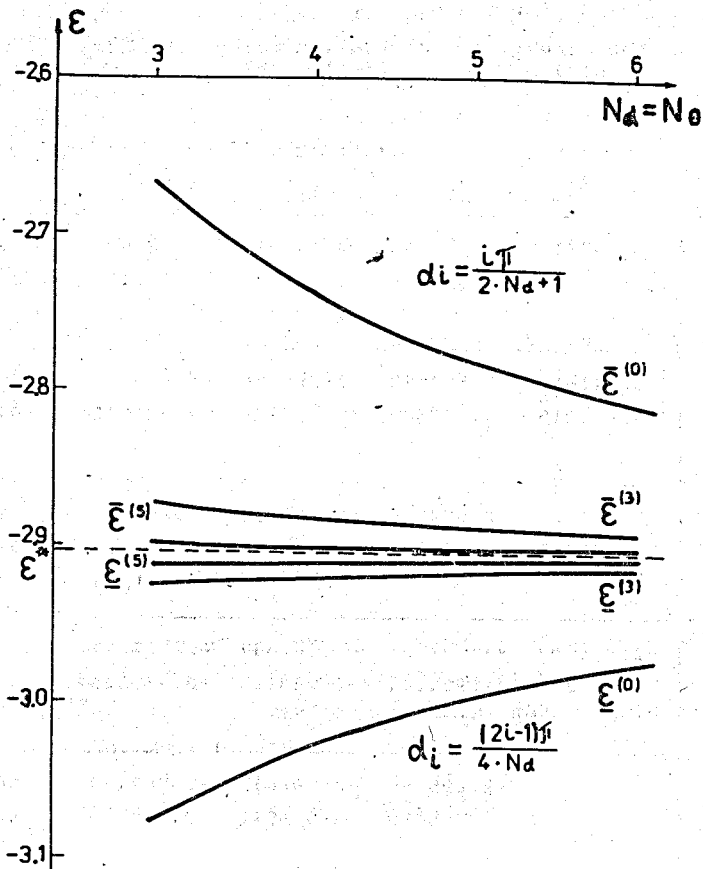


Fig.1

function) in the case $N_\alpha = N_\theta = 6, R_m = 8, h_R = 0.05$ required approximately 1CPU hour of this computer. The above-mentioned calculations (of the lowest two eigenvectors) by the method of finite difference required 16CPU hours on IBM 3081/4/.

5. CONCLUSION

In our opinion, two circumstances make the method attractive for solving different three-dimensional problems in atomic and nuclear physics. The first is a sufficiently simple algorithm for the generation of the matrix $V_{ij}(R)$ of the system of equations (16), the nondiagonal part of which can be represented as $V_{ij}^{nond}(R) = C_{ij} \cdot R^{-2}$ and does not require to calculate it at every

Table 2

The convergence of the expansion (6) on functions (14) (case (11)) for the helium-atom binding energy $E(N_\alpha, N_\theta)$

$N_\alpha \backslash N_\theta$	3	4	5
5	-2.931352	-2.922955	-2.919205
7	-2.923608	-2.915414	-2.911519
9	-2.921362	-2.913359	
11	-2.920748		

point of R . The second is a sufficiently fast convergence of the expansion (6) and the possibility for obtaining both upper and lower approximations to the binding energy of the system. We have analysed the use of different sets of points Ω_i to achieve this. Further possibility for this may be the choice of other splittings of the Hamiltonian $H(R, \Omega)$ into operators $h_0(\Omega)$ and $V(R, \Omega)$ (2).

We mention also that the approach does not require principal modification for solving three-dimensional problems arising in the consideration of other three-body problems.

ACKNOWLEDGEMENTS

The author is deeply indebted to Professor L.I. Ponomarev for stimulating discussions and support, Drs A. Adomczak, L. Bogdanova, M. Faifman, M. Kaschiev, V.I. Korobov, V.A. Kuzmin, S.I. Vinitsky and J. Wozniak for fruitful discussions.

REFERENCES

1. V.S. Melezhik. JINR Preprint D4-89-241, Dubna, 1989; accepted for publication in J. Comp. Phys.
2. K. Frankowski and C.L. Pekeris. Phys. Rev. **146** (1966) 46; **150** (1966) 366.
3. D.E. Freund, B.D. Huxtable and J.D. Morgan III, Phys. Rev. **29** (1984) 980.
4. F.S. Levin and J. Shertzer. Phys. Rev. **A32** (1985) 3285.

5. I.L.Hawk and D.L.Hardcastl.Comput.Phys.Commun.16 (1979)159.
6. I.S.Berezin and N.P.Zhidkov.Numerical Methods.(In Russian) V1,Nauka (Moscow,1959).
7. J.V.Lill,G.A.Parker and J.C.Light.Chem.Phys.Lett.89 (1982)483;
J.C.Light,I.P.Hamilton and J.V.Lill.J.Chem.Phys.82 (1985)1400.
8. W.Yang and A.C.Peet.Chem.Phys.Lett.153 (1988)98.
9. R.A.Friesner.Chem.Phys.Lett.116 (1985)39.
10. V.S.Melezhik.J.Comp.Phys.65 (1986)1.
11. V.S.Melezhik,I.V.Puzynin,T.P.Puzynina and L.N.Somov.
J.Comp.Phys.54 (1984)221.
12. E.P.Zhidkov,G.I.Makarenko and I.V.Puzynin.Part.Nucl.4(1)
(1978)127.
13. V.A.Fock.Izv.Akad.Nauk SSSR Ser.Fiz.18 (1954)161;Norske
Vidensk.Selsk.Forh.31 (1958)138.
14. A.A.Samarsky.Theory of Difference Schemes.(In Russian)
Nauka,Moscow,1977.
15. M.Abramovitz and I.Stigan.Handbook of Mathematical Functions.
Dover publications,Inc.,New York,1964.

Received by Publishing Department
on April 25, 1990.