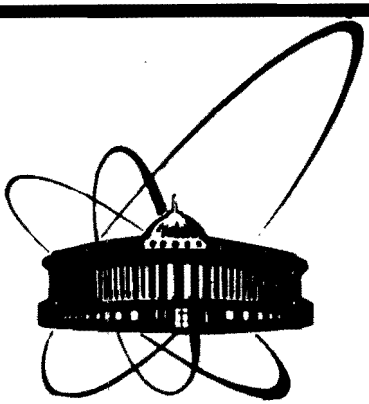

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E4-88-404

A.G.Abrashkevich*, S.I.Vinitsky, V.A.Rostovtsev

SOLVING PROBLEMS ON HYDROGEN ATOM IN ELECTRIC FIELD BY MEANS OF REDUCE

Submitted to the International Symposium on Symbolic and Algebraic Computation, July 4-8, 1988, Roma, Italy.

* Uzhgorod State University, Uzhgorod, USSR

1988

1. In recent years, atom + field systems have been intensi - vely studied both theoretically and experimentally, see, for in - stance, review [1]. For a theoretical description it is first necessary to construct a perturbative theory (PT). The calculation by PT is conveniently made by the REDUCE system described in [2].

In our previous papers ([3,4]) we made use of the system for calculating the energies and wave functions of a hydrogen atom in an inhomogeneous electric field. In this note (as well as in preliminary note [9]), we shall consider a homogenious field for simplicity. Our purpose is to demonstrate the possibilities of the REDUCE for solving PT problems in quantum mechanics in the language of the dynamic-symmetry group. Recall that for the hydrogen atom with no field it is the SO(4) group introduced by Fok ([5]).

2. Our approach ([6]) is based on the dynamical group SO(4,2) (see [7]) which takes the external field into account as well. A unitary irreducible representation of the algebra SO(4) is connected by a dilatation transformation with wave functions of the discrete spectrum of a hydrogen atom, and perturbations of a polynomial form are directly expressed through generators of the algebra SO(4,2). Therefore, the solution of an initial spectral problem is reduced to a pure algebraic procedure well adjusted for implementation with the help of REDUCE. Unlike standard PT, here corrections to eigenfunctions in each finite order are expressed by a linear combination of a finite number of the basis functions of a unitary irreducible representation of SO(4,2). Corrections to the eigenvalues and coefficients of that combination are given by polynomials of eigenvalues of a complete set of commuting generators of the SO(4,2) algebra characterizing the unperturbed problem. For the Stark effect such a set $[n\ \Delta\ m]$ is defined by parabolic quantum numbers $[n_1\ n_2\ m]$: $n = n_1+n_2+m+1$ is a principal quantum number; $-\Delta = n_2 - n_1$ is a third projection of the Runge-Lenz vector; and m is a third projection of the electron orbital moment on field $\vec{F}$.

3. This note presents a short account of an algebraic PT and the text of the program "STARK". This program implements the PT in the source language of the REDUCE system. It allows us to obtain, in k-th order of PT, analytic expressions in the form of polynomials of three variables n, Δ, and m for corrections to the energy and for coefficients $b_{st}^{(k)}$, $-2k \le s, t \le 2k$ of the linear combination of basis functions corresponding to the k-th correction to the wave function

$$\psi_{n_1 n_2 m}^{(k)} = \sum_{s=-2k}^{2k} \sum_{t=-2k}^{2k} b_{st}^{(k)} |st\rangle$$

where $|st\rangle = |n_1+s,\ n_2+t,\ m\rangle$ is a state vector in k-th order of PT. These corrections appear when a hydrogen atom with charge Z_a being in an arbitrary state $|n_1 n_2 m\rangle$ is placed in a homogenious field F. Hereafter we use atomic units. As a test we present the expressions for $E^{(p)}$ and $b_{st}^{(p)}$, p=1,2. The proposed procedure may be generalized to other polynomial fields and other systems, for instance, to a quantum-mechanical oscillator in an external polynomial field. In the latter case it is necessary to use an oscillator representation of the group SO(4,2) or SO(2,1) ([7]).

When REDUCE is applied to problems like these, the need is arising to define an action of operators $\hat{f}(r,z)$ of two independent variables r,z on a state vector $\langle r,z|st\rangle = KET(s,t)$. Unlike the article [8], where similar operation in two-dimensional Gross-Neveu's model is defined on the basis state $|0\rangle$, we define the action of an operator on an arbitrary state $|n_1\ n_2\ m\rangle$. It allows us to realize degenerate PT shemes.

4. Let us introduce the notation and recall basis properties of the group SO(4,2). The Lie algebra SO(4,2) is formed by 15 generators $L_{\alpha\beta} = -L_{\beta\alpha}$, where $\alpha,\beta = 1,\ldots,6$:

$$[L_{\alpha\beta}, L_{\alpha\gamma}] = i g_{\alpha\alpha} L_{\beta\gamma}, \quad g_{\alpha\alpha} = (1111\text{-}1\text{-}1). \qquad (1)$$

In the x-representation $L_{\alpha\beta}$ are given by the relations (i,j,k=1,2,3):

$$L_{ij} = x_i p_j - x_j p_i \equiv \varepsilon_{ijk} L_k$$

$$L_{i4} = 1/2(x_i \vec{p}^2 + 2ip_i - 2\vec{x}\vec{p}p_i - x_i) \equiv A_i$$

$$L_{i5} = 1/2(x_i \vec{p}^2 + 2ip_i - 2\vec{x}\vec{p}p_i + x_i) \qquad (2)$$

$$L_{46} = 1/2(r\vec{p}^2 - r), \qquad L_{56} = 1/2(r\vec{p}^2 + r),$$

$$L_{45} = -i(1 + \vec{x}\vec{p}), \qquad L_{i6} = -r_i,$$

where $p_k = -i\,\partial/\partial x_k$, L_k and A_k are components of the momentum, orbital moment and the Runge-Lenz vector of the electron, respectively, $\vec{x} = (x_1 x_2 x_3)$ are its coordinates, $r = (x_1^2 + x_2^2 + x_3^2)^{1/2}$. The operators (2) act in the Hilbert space of functions with the scalar product

$$\langle f|g\rangle = \int d^3x\, f^*(\vec{x}) r^{-1} g(\vec{x}), \tag{3}$$

with respect to which they are self-conjugate. For the Stark effect, we choose the basis to be formed of eigenfunctions of three commuting operators L_{56}, L_{34} и L_{12} :

$$\begin{aligned} L_{56}\,|\,n_1\,\bar{n}_2\,m\rangle &= n\,|\,n_1\,\bar{n}_2\,m\rangle \\ L_{34}\,|\,n_1\,\bar{n}_2\,m\rangle &= (n_2 - n_1)|\,n_1\,\bar{n}_2\,m\rangle \\ L_{12}\,|\,n_1\,\bar{n}_2\,m\rangle &= m\,|\,n_1\,\bar{n}_2\,m\rangle\ . \end{aligned} \tag{4}$$

Explicitly, the basis functions $\langle\vec{x}|n_1\,\bar{n}_2\,m\rangle$ are given in [6]. They differ from the Coulomb functions of the hydrogen atom by normalization and in that the argument does not depend on the $\sqrt{-2E^{(0)}}$ - energy of an unperturbed atom, $E^{(0)} = -z_a/(2n^2)$, i.e. those functions form the Sturm basis with a uniform asymptotics. Their normalization is determined by the scalar product (3), however, we make use of nonnormalized functions

$$\begin{aligned} |n_1 n_2 m\rangle &= C^{-1}_{n_1 n_2 m}\,|\,n_1 \bar{n}_2 m\,\rangle \\ C_{n_1 n_2 m} &= \sqrt{2}\,\{\,n_1!\;n_2!/\,[(n_1+m)!(n_2+m)!]\,\}^{1/2}. \end{aligned} \tag{5}$$

The action of the operators L_{46} и L_{56} in this basis is defined by the relations

$$\begin{aligned} (L_{46}-L_{35})|n_1 n_2 m\rangle &= (n_1+m)|n_1-1\;\;n_2\;\;m\rangle + (n_1+1)|n_1+1\;\;n_2\;\;m\rangle \\ (L_{46}+L_{35})|n_1 n_2 m\rangle &= (n_2+m)|n_1\;\;n_2-1\;\;m\rangle + (n_2+1)|n_1\;\;n_2+1\;\;m\rangle, \end{aligned} \tag{6}$$

This definition allows us to avoid half-integer degrees of poly - nomials when we set the action of the operators L_{46} и L_{35} on the basis, to diminish the number of algebraic substitutions, and to shorten the run time considerably.

The energy E of the hydrogen atom in uniform electric field F may be represented by the expansion

$$E(F) = E^{(0)} + \sum_{k=1} F^k E^{(k)}. \tag{7}$$

Then the Scrödinger equation is reduced to the following equation for the state vector $|\phi\rangle$ ([8]):

$$\left\{ L_{56} - n - \sum_{k=1} F^k V^{(k)}(x_3,r) \right\} |\phi\rangle = 0 \tag{8}$$

where

$$\begin{aligned} V^{(1)}(x_3,r) &= \left\{ E^{(1)}R - rZ \right\} n/Z_a \\ V^{(2)}(x_3,r) &= \left\{ E^{(k)}r \right\} n/Z_a \\ x_3 &= (L_{35}-L_{34})n/Z_a, \qquad r = (L_{56}-L_{46})n/Z_a. \end{aligned}$$

Accordingly, the solution to (8) is looked for in the form

$$|\phi\rangle = |n_1\,\bar{n}_2\,m\rangle + \sum_{k=1} |\phi^{(k)}\rangle F^{(k)}, \tag{9}$$

and instead of (8) we get the system of inhomogeneous equations for $E^{(k)}$ and $|\phi\rangle$:

$$\begin{aligned} &L(n)|n_1\;n_2\;m\rangle = \left\{L_{56}-n\right\}|n_1\;\bar{n}_2\;m\rangle = 0 \\ &\ldots \\ &L(n)|\phi^{(k)}\rangle = V^{(k)}(x_3,r)|n_1\;\bar{n}_2\;m\rangle + \sum_{p=1}^{k-1} V^{(k-p)}(x_3,r)|\phi^{(p)}\rangle \equiv f^{(k)} \end{aligned} \tag{10}$$

Taking into consideration the relations (4), (6) and the polynomial form of $V^{(k)}$, we expand the right-hand sides of $f^{(k)}$ and corrections $|\phi^{(k)}\rangle$ over the state vector

$$|st\rangle = |n_1+s\;\;n_2+t\;\;m\rangle C_{n_1 n_2 m}, \tag{11}$$

normalized so that $|00\rangle = |n_1 n_2 m\rangle$:

$$f^{(k)} = \sum_{s=-2k}^{2k}\sum_{t=-2k}^{2k} f^{(k)}_{st}|st\rangle = V^{(k)}(x_3,r)|00\rangle + \sum_{p=1}^{k-1} V^{(k-p)}|\phi^{(p)}\rangle\ , \tag{12}$$

$$|\phi^{(k)}\rangle = \sum_{s=-2k}^{2k}\sum_{t=-2k}^{2k} b^{(k)}_{st}|st\rangle, \quad b^{(k)}_{00} = 0, \quad b^{(k)}_{s\,-s} = 0. \tag{13}$$

With the orthogonality condition of functions $|st\rangle$ in the sence of (3) and the relation (4): $L(n)|st\rangle = (s+t)|st\rangle$, we obtain, instead of (10),

$$\begin{aligned} &(s+t)b^{(k)}_{st}|st\rangle = f^{(k)}_{st}|st\rangle \\ &f^{(k)}_{00} = 0 \end{aligned} \tag{14}$$

In each order, starting from the first one, we subsequently obtain $E^{(k+1)}$ and $b_{st}^{(k+1)}$, by solving an algebraic equation for

$$f_{00}^{(k+1)}(E^{(k+1)}, E^{(p)}, b_{st}^{(p)}, 1\le p\le k) = 0 \qquad (15)$$

$$b_{st}^{(k+1)} = (s+t)^{-1} f_{st}^{(k+1)}(E^{(p)}, 1\le p\le k+1, b_{st}^{(l)}, 1\le l\le k) \qquad (16)$$

The initial conditions for the recurrence procedure (15), (16) are given by

$$E^{(0)} = -Z_a^2/(2n^2), \quad b_{st}^{(0)} = 0 \qquad (17)$$

Note that the procedure (15)-(17) fixes the eigenvector $|\phi\rangle$ up to the normalization. In the considered variant of PT the free parameter $b_{00}^{(t)}$ was taken zero. When necessary, the obtained vector $|\phi\rangle$ may be easily normalized with the use of the definition (3).

In this work, the procedure (15)-(17) is realized in the source language of the computer algebra system REDUCE as the program STARK. This program is adjuced in Appendix together with modifications necessary for inhomogenious field case. In the programm we use the following notation:

$$X3 \equiv x_3, \quad R \equiv r, \quad F \equiv f^{(k)}, \quad EE \equiv E^{(k)}$$
$$B \equiv b_{st}^{(k)}, \quad KET(st) \equiv |st\rangle$$
$$N \equiv n, \quad N1 \equiv n_1, \quad N2 \equiv n_2, \quad M \equiv m, \quad D \equiv \Delta.$$

Note that in the program the set of parabolic numbers [N1 N2 M] in the course of calculations is replaced by an equivalent set [N D M].

Appendix

Program STARK

```
COMMENT AT FIRST ONE NEEDS TO READ IN THIS PROGRAM FILE;

OPERATOR X3,R,F,B,EE,KET; NONCOM X3,R;

COMMENT CALCULATE THE PERTURBATION IN THE K-TH ORDER;
PROCEDURE V(K,X,Y);
   IF K < 1 THEN 0 ELSE IF K = 1 THEN
                              SUB(X1=X,Y1=Y,EE(1)*Y1-Y1*X1)
                         ELSE SUB(Y1=Y,EE(K)*Y1);
```



```
COMMENT CALCULATE THE RIGHT HAND SIDE OF THE ALGEBRAIC EQUATION
        IN K-TH ORDER;
FOR ALL K LET F(K)=
   N/ZA*(V(K,X3,R)*KET(0,0) +
      FOR P1:=1:K-1 SUM V(K-P1,X3,R)*(FOR S:=-2*P1:2*P1 SUM
            FOR TT:=-2*P1:2*P1 SUM B(P1,S,TT)*KET(S,TT)));

COMMENT FORMAL SUBSTITUTIONS;
LET X3=X3(), R=R();
FOR ALL X,Y LET X3()*KET(X,Y)=X3(X,Y), R()*KET(X,Y)=R(X,Y);
FOR ALL X,Y LET R(X,Y)=((N+X+Y)*KET(X,Y)-
                        1/2*((X+N1+MD)*KET(X-1,Y)+
                             (X+N1+1)*KET(X+1,Y)+
                             (Y+N2+MD)*KET(X,Y-1)+
                             (Y+N2+1)*KET(X,Y+1)))*N/ZA;
FOR ALL X,Y LET X3(X,Y)=(1/2*(-(X+N1+MD)*KET(X-1,Y)-
                               (X+N1+1)*KET(X+1,Y)+
                               (Y+N2+MD)*KET(X,Y-1)+
                               (Y+N2+1)*KET(X,Y+1))-
                              (Y-X-D)*KET(X,Y))*N/ZA;

COMMENT CALCULATE THE ENERGY AND EXPANSION COEFFICIENTS OF THE
        STATE VECTOR IN K-TH ORDER;
ARRAY C(1);
PROCEDURE FK(K);
   BEGIN SCALAR U,U1,U2;
      U:=F(K); U1:=DEN U; U:=NUM U;
      COEFF(U,KET(0,0),C);
      U2:=C(1);
      COEFF(U2,EE(K),C);
      U2:=-U2/C(1)+EE(K);
      WRITE EE(K):=U2;
      FOR I:=-2*K:2*K DO
         FOR J:=-2*K:2*K DO
            <<U2:=IF COEFF(U,KET(I,J),C) NEQ 0 THEN C(1)/U1
                  ELSE 0;
              IF (I+J) NEQ 0 THEN WRITE B(K,I,J):=U2/(I+J)
                ELSE WRITE B(K,I,J):=0>>
   END;
   COMMENT TRANSFORM NUMBERS N1, N2 INTO N,D,M;
   LET N1=(N+D-M-1)/2, N2=(N-D-M-1)/2;
   FOR ALL X,Y,Z SUCH THAT X <= 0 LET B(X,Y,Z)=0;
```

```
END OF THE PROGRAM FILE;

COMMENT INPUT OF INITIAL DATA - READ THE DATA UP TO (K-1)-TH ORD;
IN STARKIN;

COMMENT OUTPUT OF THE RESULTS UP TO K-TH ORDER TO A FILE. SUBSTI-
        TUTE AN INTEGER TO PARAMETER K;
LINELENGTH(65); OFF NAT,ECHO; OUT STARKOUT;
FK(K);
WRITE "END"; SHUT STARKOUT; ON NAT,ECHO;

END OF RUN;

COMMENT ***** THE CHANGES NEEDED TO FORM PROGRAM "MULT" (INHOMO-
        GENIOUS FIELD CASE);
COMMENT ADD THE LINE:              ;
OPERATOR FAC,A;
COMMENT ADD TWO DEFINITIONS:       ;
FOR ALL X LET FAC(X)=FOR I:=1:X PRODUCT I;
PROCEDURE P(N,X);
   IF N<0 THEN 0 ELSE IF N=0 THEN 1 ELSE IF N=1 THEN X
                     ELSE ((2*N-1)*X*P(N-1,X)-(N-1)*P(N-2,X))/N;
COMMENT REPLACE V(K,X,Y) PROCEDURE DEFINITION :         ;
PROCEDURE V(K,X,Y);
   IF K<=1 THEN 0 ELSE SUB(X1=X,Y1=Y,EE(K)*Y1+
                               ZB*(-1)**(K-1)*Y**K*P(K-1,X1/Y1));

COMMENT REPLACE THE DEFINITION OF F(K);
FOR ALL K LET F(K)= N/ZA*(V(K,X3,R)*KET(0,0) +
    FOR P1:=1:K-1 SUM V(K-P1,X3,R)*
        ((FOR S:=-P1:P1 SUM A(P1,S,-S)*KET(S,-S)) +
            FOR S:=-P1:P1 SUM
              FOR TT:=-P1:P1 SUM B(P1,S,TT)*KET(S,TT)));
 COMMENT REPLACE FK(K) PROCEDURE DEFINITION :            ;
 PROCEDURE FK(K);
    BEGIN SCALAR U,U1,U2,K1,Z,Z1;
       U:=F(K); U1:=DEN U; U:=NUM U; K1:=K-2;
       COEFF(U,KET(0,0),C); U2:=C(1);
       COEFF(U2,EE(K),C); U2:=-U2/C(1)+EE(K);
       WRITE EE(K):=U2;
       IF K1>0 THEN
          FOR S:=-K1:K1 DO
```



```
             <<Z:=S; Z1:=-S; U1:=U1*DEN(U); U:=NUM U;
               U2:=IF COEFF(U,KET(Z,Z1),C) = 0 THEN 0 ELSE C(1);
               U2:=IF COEFF(U2,A(K1,Z,Z1),C) = 0 THEN 0
                     ELSE -U2/C(1)+A(K1,Z,Z1);
               WRITE A(K-2,S,-S):=U3>>;
       FOR I:=-K:K DO
          FOR J:=-K:K DO
             <<U2:=IF COEFF(U,KET(I,J),C) = 0 THEN 0 ELSE C(1)/U1;
               IF (I+J) NEQ 0 THEN WRITE B(K,I,J):=U2/(I+J)
                 ELSE WRITE B(K,I,J):=0>>
    END;

COMMENT ADD THE CONDITIONS:                ;
FOR ALL X,Y,Z SUCH THAT X<=0 LET A(X,Y,Z)=0;
FOR ALL X,Y,Z SUCH THAT X=1 LET B(X,Y,Z)=0;

COMMENT CHANGE THE FILE NAMES IN COMMANDS "IN","OUT" & "SHUT";
COMMENT ***** END OF CHANGES ***** ;

COMMENT EXAMPLES OF RESULTS AS THEY HAVE WRITTEN TO THE FILE
        STARKOUT;

EE(1) := (3*D*N)/(2*ZA)$

B(1,0,2) := (N**3*(D**2 + 2*D*M -2*D*N -4*D + M**2 - 2*M*N - 4*M
 + N**2 + 4*N + 3))/(32*ZA**3)$

EE(2) := (N**4*(3*D**2 + 9*M**2 -17*N**2 -19))/(16*ZA**4)$

B(2,0,2)  :=  (N**6*(D**4  +  2*D**3*M  +  2*D**3*N  +  4*D**3
 + D**2*M**2 + 6*D**2*M*N + 12*D**2*M - 3*D**2*N**2 - 6*D**2*N
 - 5*D**2 + 4*D*M**2*N + 8*D*M**2 + 12*D*M*N + 16*D*M - 4*D*N**3
 -36*D*N**2 - 92*D*N - 72*D+ 4*M**2*N**2 + 22*M**2*N + 24*M**2
 - 8*M*N**3 - 60*M*N**2 - 136*M*N - 96*M + 4*N**4 + 38*N**3
 + 124*N**2 + 162*N + 72))/(128*ZA**6)$
```

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Received by Publishing Department
on June 6, 1988.

Абрашкевич А.Г., Виницкий С.И., Ростовцев В.А. Е4-88-404

Решение задач об атоме водорода
в электрическом поле с использованием системы РЕДЬЮС

Обсуждается методика решения задач теории возмущений квантовой механики на языке группы динамической симметрии квантовой механики с помощью системы компьютерной алгебры РЕДЬЮС. Приведена программа вычисления в аналитическом виде энергии и волновых функций атома водорода в электрическом поле в произвольном порядке теории возмущений.

Работа выполнена в Лаборатории вычислительной техники и автоматизации ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1988

Abrashkevich A.G., Vinitsky S.I., Rostovtsev V.A.

Solving Problems on Hydrogen Atom E4-88-404
in Electric Field by Means of REDUCE

A technique of solving perturbation theory problems of quantum mechanics in the language of the dynamic symmetry group by means of REDUCE computer algebra system is discussed. The program for analytical calculation of energy and wave functions of hydrogen atom in an electric field in arbitrary order of the perturbation theory is presented.

The investigation has been performed at the Laboratory of Computing Techniques and Automation, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna 1988