# Calculations of the Stark effect in hydrogen atoms by using the dynamical symmetry O(2, 2)×O(2)

S. P. Alliluev and I. A. Malkin

*Moscow Physico-technical Institute*

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The Stark effect in hydrogen is treated by perturbation theory. The matrix elements of the perturbation are calculated by using the dynamical symmetry group of the hydrogen atom, and the perturbation-theory series is summed to fourth-order in the field, inclusively. The results are compared with previous calculations.

## 1. INTRODUCTION

The Stark effect in the hydrogen atom—the splitting of the energy levels (and consequently of the spectral lines) in a constant and homogeneous external electric field—has been a classical problem for a long time. After the first articles[1,2] in which the linear Stark effect (first-order with respect to the electric field intensity) was derived, articles followed in which the quadratic[3-7] and cubic[8] Stark effects were derived. The most complete and detailed calculations of the Stark effect based on perturbation theory are contained in the article by Basu,[9] where a calculation of the terms of fourth-order in the field intensity is presented and calculations of the lower order terms are repeated. We note that the corrections to the ground state (neglecting ionization) are derived in[10,11] with terms up to tenth order in the field taken into consideration. Numerical calculations of the Stark effect based on the quasiclassical approximation are contained in[12]. The numerical solution (without making any approximations) of the Stark-effect problem for the ground state of the hydrogen atom is considered in[13]. The method of standard problems is utilized in[14], where an expression is obtained for the energy of any arbitrary level to second-order in the field, and an expression is given for the corresponding width Γ. With the aid of the precise Bohr-Sommerfeld quantization rule, an expression correct to fourth order in the field (for arbitrary n) is derived in[15] for the energy. A purely algebraic calculation of the Stark effect, using the dynamical O(4, 2) symmetry of the hydrogen atom,[16-18] was recently carried out in[19].

In the present article we propose a method based on the application of perturbation theory, which substantially utilizes the dynamical symmetry (noninvariance group) of the free hydrogen atom within the framework of the conventional procedure for solving the problem.[20,21] The proposed method is significantly more economical than the usual method, a particularly important factor in connection with the calculation of the fourth-order approximation. We obtain the expression for the energy of any level correct to terms of fourth-order in the field. The first three corrections agree with the results of previous calculations. However, the fourth-order approximation differs from the result calculated by Basu[9] (there is an obvious arithmetic error in Basu's answer since the fourth-order correction to the ground state level, $E^{(4)}_{\text{ground}} = -(3555/64)\epsilon^4$ in atomic energy units, which has been obtained by many authors,[10,11,15,19] does not follow from it) and it also does not agree with the result obtained by Bekenstein and Krieger[15] with the aid of the quasiclassical approximation. (See Sec. 4 of the present article for a discussion of the sources of the arithmetic errors in[9,15].)

Let us recall the standard procedure for solving the problem.[20,21] The Schrödinger equation for a hydrogen atom in an external, homogeneous electric field (directed along the z axis) has the form

$$\nabla^2\psi+2(E+1/r-\mathscr{E}z)\psi=0, \tag{1}$$

(we shall use atomic units, corrected by the reduced mass of the electron). Since we are interested in the bound states, we seek the energy in the form

$$E=-\varkappa^2/2. \tag{2}$$

Equation (1) can be separated in parabolic coordinates:[7]

$$\xi=\varkappa(r+z),\quad \eta=\varkappa(r-z),\quad \varphi=\operatorname{arctg}(y/x), \tag{3}$$

where the factor $\varkappa$ has been introduced into the definition of the parabolic coordinates for reasons of convenience. We seek $\psi$ in the form

$$\psi=F(\xi)G(\eta)e^{im\varphi}, \tag{4}$$

where m is the magnetic quantum number. We obtain the following equations for F and G:

$$\begin{gathered}\frac{d}{d\xi}\left(\xi\frac{dF}{d\xi}\right)+\left(\lambda_1-\frac{\xi}{4}-\frac{m^2}{4\xi}-\frac{\mathscr{E}}{4\varkappa^3}\xi^2\right)F=0,\\ \frac{d}{d\eta}\left(\eta\frac{dG}{d\eta}\right)+\left(\lambda_2-\frac{\eta}{4}-\frac{m^2}{4\eta}+\frac{\mathscr{E}}{4\varkappa^3}\eta^2\right)G=0.\end{gathered} \tag{5}$$

The separation constants $\lambda_1$ and $\lambda_2$ appearing in Eqs. (5) are related by the condition

$$\lambda_1+\lambda_2=1/\varkappa. \tag{6}$$

Considering each equation in (5) for fixed $\varkappa$ (and, of course, for fixed values of $|m|$ and $\mathscr{E}$) as an eigenvalue problem (the problem of determining the eigenfunctions and eigenvalues), we obtain discrete values for $\lambda_1$ and $\lambda_2$. Substituting these values into (6) we obtain a certain equation for $\varkappa$, and from the latter we can determine $\varkappa$ and E.

## 2. THE DYNAMICAL SYMMETRY GROUP O(2, 1) AND THE SOLUTION OF THE SEPARATED EQUATIONS

Since Eqs. (5) can be obtained from one another by replacing $\xi$ by $\eta$ and $\mathscr{E}$ by $-\mathscr{E}$, it is sufficient to investigate only the first of these, which we rewrite in the following form:

$$\left(\hat{M}_0+\frac{\mathscr{E}}{4\varkappa^3}\xi^2\right)F=\lambda F, \tag{7}$$

(we temporarily omit the subscript 1 of $\lambda$), where $\hat{M}_0$ denotes the operator

$$\hat{M}_0 \equiv -\frac{d}{d\xi}\left(\xi\frac{d}{d\xi}\right)+\frac{\xi}{4}+\frac{m^2}{4\xi}. \tag{8}$$

As one can easily see, the operator (8) is self-adjoint and positive-definite. One can regard Eq. (7) as the problem of finding the eigenvalues and eigenfunctions of the operator $\hat{M}_0$, which is perturbed by the small operator

$$\hat{V}=\frac{\mathscr{E}}{4\varkappa^3}\xi^2. \tag{9}$$

Let us investigate the unperturbed problem. In addition to the operator $\hat{M}_0$ we also consider the two operators

$$\begin{gathered}\hat{M}_1\equiv\frac{\xi}{2}-\hat{M}_0=\frac{d}{d\xi}\left(\xi\frac{d}{d\xi}\right)+\frac{\xi}{4}-\frac{m^2}{4\xi},\\ \hat{M}_2\equiv i\left(\xi\frac{d}{d\xi}+\frac{1}{2}\right).\end{gathered} \tag{10}$$

The operators (8) and (10) satisfy the commutation relations

$$[\hat{M}_1,\hat{M}_2]=-i\hat{M}_0,\quad [\hat{M}_0,\hat{M}_1]=i\hat{M}_2,\quad [\hat{M}_2,\hat{M}_0]=i\hat{M}_1, \tag{11}$$

that is, they generate the algebra of the noncompact group O(2, 1). The Casimir operator constructed from the operators (8) and (10) is identically equal to the constant

$$\hat{C}\equiv\hat{M}_1^2+\hat{M}_2^2-\hat{M}_0^2=(1-m^2)/4, \tag{12}$$

which

$$C\equiv(1-m^2)/4. \tag{12a}$$

Let us find the eigenvalue spectrum of the operator (8):

$$\hat{M}_0|k\rangle=k|k\rangle. \tag{13}$$

(The eigenvector corresponding to the eigenvalue $k$ is denoted by $|k\rangle$.) A minimum eigenvalue $k_{\min}$ exists in virtue of the positive-definiteness of the operator $\hat{M}_0$. It follows from Eqs. (11) that the operators

$$\hat{M}_\pm=\hat{M}_1\pm i\hat{M}_2 \tag{14}$$

satisfy the commutation relations

$$[\hat{M}_0,\hat{M}_\pm]=\pm\hat{M}_\pm. \tag{15}$$

In analogy with ordinary angular momentum, we can assert that the relation

$$\hat{M}_-|k_{min}\rangle=0. \tag{16}$$

holds for the eigenvector corresponding to the minimum eigenvalue $k_{\min}$. Applying the operator $\hat{M}_+$ to Eq. (16) and using Eqs. (11) and (12), we obtain

$$\begin{aligned}\hat{M}_+\hat{M}_-|k_{min}\rangle&=(\hat{M}_1^2+\hat{M}_2^2-\hat{M}_0)|k_{min}\rangle=(\hat{M}_1^2+\hat{M}_2^2-\hat{M}_0^2+\hat{M}_0^2-\hat{M}_0)|k_{min}\rangle\\ &=\left(\frac{1-m^2}{4}+k_{min}^2-k_{min}\right)|k_{min}\rangle=0,\end{aligned} \tag{17}$$

from where it follows that

$$k_{min}^2-k_{min}+(1-m^2)/4=0. \tag{18}$$

Solving this quadratic equation, we find $k_{\min}=\frac{1}{2}\pm|m|/2$. In virtue of the positive definiteness of the operator (8), we should only keep the root

$$k_{min}=(|m|+1)/2. \tag{19}$$

out of the two roots of Eq. (18), It follows from the commutation relations (15) that the distance between neighboring eigenvalues of $\hat{M}_0$ is equal to unity. Thus, we have a spectrum of the following type for $k$:

$$k=p+(|m|+1)/2,\quad p=0,1,2,\ldots \tag{20}$$

which naturally agrees with the eigenvalue spectrum of the unperturbed separation constants:[20,21]

$$\lambda_1^{(0)}=n_1+(|m|+1)/2,\quad \lambda_2^{(0)}=n_2+(|m|+1)/2,\quad n_1,n_2=0,1,2,\ldots \tag{21}$$

where $n_1$ and $n_2$ are the so-called parabolic quantum numbers. Substitution of (21) into condition (6) gives the Bohr formula for the energy levels of the free hydrogen atom

$$E^{(0)}=-1/2(n_1+n_2+|m|+1)^2. \tag{22}$$

Relations (13), (19), and (20) describe a representation of the noncompact group O(2, 1). This infinite-dimensional representation is irreducible, which in particular becomes apparent in the fact that the Casimir operator $\hat{C}$ (given by expression (12)) is equal to a constant. Thus, the dynamical symmetry of the problem (which is obviously of the form O(2, 1) × O(2, 1) × O(2) and is locally isomorphic to the group O(2, 2) × O(2) and which is a subgroup of the total dynamical group O(4, 2) of the problem) enables us to derive the energy spectrum of the unperturbed problem by purely algebraic methods.

In order to utilize the formulas of perturbation theory we need the matrix elements of the perturbation (9), that is, in the final analysis we need to know the matrix elements of $\xi^2$. We note that the relation

$$\xi=2\hat{M}_0+2\hat{M}_1=2\hat{M}_0+\hat{M}_++\hat{M}_-, \tag{23}$$

follows from (10), and thus the matrix elements of $\xi$ can be expressed in terms of the matrix elements of the generators of the algebra O(2, 1). These matrix elements can easily be found from the commutation relations (15) and from formulas (12) and (13). The nonvanishing matrix elements of the operators $\hat{M}_0$, $\hat{M}_+$, and $\hat{M}_-$ take the form

$$\begin{gathered}\langle k|\hat{M}_0|k\rangle=k,\\ \langle k+1|\hat{M}_+|k\rangle=(k^2+k+C)^{1/2},\\ \langle k-1|\hat{M}_-|k\rangle=(k^2-k+C)^{1/2},\end{gathered} \tag{24}$$

(the derivation of relations (24) is completely analogous to the derivation of expressions for the matrix elements of the usual angular momentum operators). From Eqs. (23) and (24) one can easily obtain the nonvanishing matrix elements of $\xi$:

$$\begin{gathered}\langle k|\xi|k\rangle=2k,\\ \langle k+1|\xi|k\rangle=(k^2+k+C)^{1/2},\\ \langle k-1|\xi|k\rangle=(k^2-k+C)^{1/2},\end{gathered} \tag{25}$$

and also the matrix elements of $\xi^2$ which are of immediate interest to us:

$$\begin{gathered}\langle k|\xi^2|k\rangle=6k^2+2C,\\ \langle k+1|\xi^2|k\rangle=2(2k+1)(k^2+k+C)^{1/2},\\ \langle k-1|\xi^2|k\rangle=2(2k-1)(k^2-k+C)^{1/2},\\ \langle k+2|\xi^2|k\rangle=[(k^2+3k+C+2)(k^2+k+C)]^{1/2},\\ \langle k-2|\xi^2|k\rangle=[(k^2-3k+C+2)(k^2-k+C)]^{1/2}.\end{gathered} \tag{26}$$

Naturally (26) coincides (to within an unimportant phase factor) with the expression for the matrix elements of $\xi^2$ which is obtained by using the explicit form of the unperturbed eigenfunctions of Eq. (5),[20] provided that the relations between $k_1$ and $k_2$ and the parabolic quantum numbers $n_1$ and $n_2$ are taken into consideration:

$$k_1=n_1+\frac{|m|+1}{2},\quad k_2=n_2+\frac{|m|+1}{2}. \tag{27}$$

Thus, the noninvariance group O(2, 1) enables us to also obtain the matrix elements of the perturbation by purely algebraic methods.

The matrix element

$$\langle k+\mu|\xi^2|k+\nu\rangle, \tag{28}$$

where $\mu$ and $\nu$ are certain integers, is frequently encountered in the perturbation-theory formulas. We note that expression (28) does not vanish only for those values of $\mu$ and $\nu$ which do not differ by more than ±2. Let us compare this matrix element with the following:

$$\langle k-\mu|\xi^2|k-\nu\rangle. \tag{29}$$

Simple calculations show that if

$$\langle k+\mu|\xi^2|k+\nu\rangle=P(k),$$

where $P(k)$ is some function of $k$, then

$$\langle k-\mu|\xi^2|k-\nu\rangle=(-1)^{\mu+\nu}P(-k). \tag{30}$$

The symmetry property (30) of the matrix elements plays a very important role in our subsequent calculations, and it would be desirable to understand its cause. Let us consider the following transformation of our operators:

$$\hat{M}_0\to-\hat{M}_0,\quad \hat{M}_1\to-\hat{M}_1,\quad \hat{M}_2\to\hat{M}_2. \tag{31}$$

The transformation (31) does not change the commutation relations (11), and consequently it does not change (15) either. The operator

$$\xi^2=4(\hat{M}_0+\hat{M}_1)^2$$

does not change its form under the transformation (31) whereas the sign of the quantum number $k$ does change:

$$k\to-k. \tag{31a}$$

Thus, the matrix elements of the operator $\xi^2$, which is invariant under the transformation (31), can only be multiplied by a phase factor

$$\langle -k'|\xi^2|-k''\rangle=\pm\langle k'|\xi^2|k''\rangle. \tag{32}$$

The correctness of expression (32) can also be verified directly from relations (26). Expression (30) follows immediately from (32):

$$\langle k-\mu|\xi^2|k-\nu\rangle=\pm\langle -k+\mu|\xi^2|-k+\nu\rangle. \tag{33}$$

## 3. CALCULATIONS

Since all the matrix elements of $\xi^2$ are rather simple functions of $k_1$ and $|m|$ (the dependence on the quantum number $|m|$ appears in the matrix elements in the form of the combination $C = (1 - m^2)/4$) and since each order of perturbation theory contains only a finite number of terms, it is clear that the separation constants $\lambda_1$ and $\lambda_2$ can be represented in the form

$$\lambda_1=k_1+f_1(k_1,|m|)\frac{\mathscr{E}}{\varkappa^3}+f_2(k_1,|m|)\frac{\mathscr{E}^2}{\varkappa^6}+\dots, \tag{34}$$

$$\lambda_2=k_2-f_1(k_2,|m|)\frac{\mathscr{E}}{\varkappa^3}+f_2(k_2,|m|)\frac{\mathscr{E}^2}{\varkappa^6}-\dots \tag{35}$$

(the expression for $\lambda_2$ is obtained from the expression for $\lambda_1$ by replacing $k_1$ by $k_2$ and $\mathscr{E}$ by $-\mathscr{E}$, where the $f_p(k, |m|)$ are certain rather simple functions of their arguments.

Let us show that the functions $f_p(k, |m|)$ have a definite parity with respect to a change in the sign of $k$ (the parity of $f_p$ is opposite to the parity of $p$, which denotes the order of perturbation theory). Let us consider the transformation (31) of the operators. Equation (7) takes the form

$$\left(-\hat{M}_0+\frac{\mathscr{E}}{4\varkappa^3}\xi^2\right)F=\tilde{\lambda}F, \tag{7a}$$

where $\tilde{\lambda}$ is the eigenvalue corresponding to a change in the sign of $k$, that is,

$$\tilde{\lambda}=\lambda(-k,\mathscr{E}).$$

On the other hand, by comparing Eq. (7a) with (7) we have $\tilde{\lambda} = -\lambda(k, -\mathscr{E})$, that is,

$$\lambda(-k,\mathscr{E})=-\lambda(k,-\mathscr{E}). \tag{7b}$$

Representing $\lambda(k, \mathscr{E})$ in the form of the series (34) and using Eq. (7b) we obtain

$$f_p(-k,|m|)=-(-1)^p f_p(k,|m|).$$

Substituting (34) and (35) into condition (6), we obtain

$$n\left(1+A_1\frac{\mathscr{E}}{\varkappa^3}+A_2\frac{\mathscr{E}^2}{\varkappa^6}+A_3\frac{\mathscr{E}^3}{\varkappa^9}+A_4\frac{\mathscr{E}^4}{\varkappa^{12}}+\dots\right)=\frac{1}{\varkappa}, \tag{36}$$

where

$$A_p=\frac{1}{n}\{f_p(k_1,|m|)+(-1)^p f_p(k_2,|m|)\}. \tag{37}$$

By finding $\kappa$ from expression (36) and then using $E = -\kappa/2$ to find $E$ in the form of a power series in $\mathscr{E}$, we obtain

$$E=-\frac{1}{2n^2}+\gamma_1\mathscr{E}+\gamma_2\mathscr{E}^2+\gamma_3\mathscr{E}^3+\gamma_4\mathscr{E}^4+\dots, \tag{38}$$

where

$$\begin{gathered}\gamma_1=nA_1,\quad \gamma_2=n^4(A_2+{}^3/_2A_1^2),\\ \gamma_3=n^7(A_3+6A_1A_2+5A_1^3),\\ \gamma_4=n^{10}(A_4+9A_1A_3+{}^9/_2A_2^2+36A_1^2A_2+21A_1^4).\end{gathered} \tag{39}$$

A cursory examination of formulas (34)--(39) indicates that the solution of the problem in fact reduces to the determination of the functions $f_p$, $p = 1, 2, \dots$

### First-Order Perturbation Theory

The operator $\hat{M}_0$ obviously plays the role of the unperturbed Hamiltonian, and the operator (9) plays the role of the perturbation:

$$\hat{V}=\frac{\mathscr{E}}{\varkappa^3}\frac{\xi^2}{4}.$$

Taking the diagonal matrix element of the operator $\hat{V}$ and cancelling the factor $\mathscr{E}/\kappa^3$, we obtain the following expression for $f_1$:

$$f_1=\langle k|{}^1/_4\xi^2|k\rangle={}^1/_4(6k^2+2C). \tag{40}$$

### Second-Order Perturbation Theory

Using the well known formula for the second-order correction in perturbation theory and taking into consideration that the quantum number $k$ plays the role of the unperturbed energy eigenvalues, we can (cancelling out the factor $\mathscr{E}^2/\kappa^6$) write down the following expression for $f_2$:

$$16f_2={\sum_{k'}}'\frac{\langle k|\xi^2|k'\rangle^2}{k-k'}={\sum_{\mu}}'\frac{(0|\mu)^2}{-\mu}, \tag{41}$$

where we have utilized the notation

$$\langle k+\mu|\xi^2|k+\nu\rangle\equiv(\mu|\nu), \tag{42}$$

which permits us to greatly simplify the writing of subsequent formulas. The index $\mu$ in (41) takes (in principle) all integer values (positive and negative) other than zero. In expression (41) we select two terms, which differ by the sign of $\mu$, and we take their sum which we denote by the symbol $[\mu]$:

$$[\mu]\equiv\frac{(0|\mu)^2}{-\mu}+\frac{(0|-\mu)^2}{\mu}. \tag{43}$$

It is easy to see that

$$[-\mu]=[\mu]. \tag{44}$$

Recognizing that the matrix element $\langle 0|\mu\rangle$ does not vanish only for $\mu = 0, \pm1, \pm2$ and using the definition (43), we can represent the sum (41) in the form

$$16f_2=[2]+[1]. \tag{45}$$

The structure of the symbols (43) still have to be clarified. By virtue of (26) the expression $(0|\mu)^2$ is the product of two trinomials quadratic in k. Since $(0|-\mu)^2$ can be obtained from $(0|\mu)^2$ by replacing k by −k, by virtue of property (30), the expression $[\mu]$ is represented by virtue of (43) by a certain odd polynomial (of the third degree) in k, which is given by

$$[\mu] = 2\cdot\text{the part of}\left\{-\frac{(0|\mu)^2}{\mu}\right\}\text{ which is odd in k.} \tag{46}$$

Thus, the symmetry of the problem under a change in the sign of k allows us to reduce the number of calculations by a factor of four: It is sufficient to calculate half of the terms in (41) and in each term it is sufficient to determine only the coefficients associated with odd powers of k. The result of calculating the two terms in (45) and their sum leads to the following definitive expression for $f_2$:

$$f_2={}^1/_{16}(-68k^3+9m^2k-19k). \tag{47}$$

## Third-Order Perturbation Theory

Using the general formula for the third-order correction in perturbation theory[20] and the notation (42) for the matrix elements, we obtain the following expression (here the factor $\mathscr{E}^3/\kappa^9$ has been cancelled) for $f_3$:

$$\begin{aligned}64f_3&=\sum_{\mu,\nu}{}'\frac{(0|\mu)(\mu|\nu)(\nu|0)}{(-\mu)(-\nu)}-(0|0)\sum_{\nu}{}'\frac{(0|\nu)^2}{(-\nu)^2}\\&=\sum_{\mu,\nu}{}'\frac{1}{\mu\nu}(0|\mu)\{(\mu|\nu)-(0|0)\delta_{\mu,\nu}\}(\nu|0).\end{aligned} \tag{48}$$

In expression (48) we single out the sum of two terms, which differ from one another by simultaneous changes in the signs of both $\mu$ and $\nu$; in analogy with (43) we denote this sum by $[\mu\nu]$:

$$\begin{aligned}[\mu\nu]=\frac{1}{\mu\nu}\{&(0|\mu)((\mu|\nu)-\delta_{\mu,\nu}(0|0))(\nu|0)\\&+(0|-\mu)((-\mu|-\nu)-\delta_{-\mu,-\nu}(0|0))(-\nu|0)\}.\end{aligned} \tag{49}$$

We note the following obvious properties of (49):

$$[-\mu-\nu]=[\mu\nu],\quad [\nu\mu]=[\mu\nu]. \tag{50}$$

Since $(-\mu|-\nu)$ is obtained from $(\mu|\nu)$ by replacing k by −k and multiplying by the factor

$$(-1)^{\mu+\nu},$$

It is obvious that the last two terms in (49) are obtained from the first two by replacing k by −k. We also consider the fact that $(0|\mu)(\mu|\nu)(\nu|0)$ and $(0|0)(0|\mu)^2$ are the products of three quadratic trinomials in k. Thus, expression (49) is a polynomial of the sixth degree which is even in k, and for its calculation it is necessary to double that part of the sum of the first two terms in (49) which is even in k:

$$[\mu\nu]=2\cdot\text{the part of }\frac{(0|\mu)\{(\mu|\nu)-(0|0)\delta_{\mu,\nu}\}(\nu|0)}{\mu\nu}.\quad\text{which is even in k.} \tag{51}$$

Owing to the properties of the matrix elements of $\xi$, expression (48) reduces to the sum of five symbols of the type defined by (49):

$$64f_3=[22]+[21]+[12]+[11]+[1-1]. \tag{52}$$

Since the equality

$$[12]=[21],$$

holds by virtue of (50), in order to evaluate (52) it is actually only necessary to calculate four expressions of the form (51). The result of the appropriate calculations leads to the following definitive expression for $f_3$:

$$f_3={}^1/_{64}(1500k^4-258m^2k^2+918k^2+{}^{11}/_4m^4-{}^{71}/_2m^2+{}^{131}/_4). \tag{53}$$

The following interesting property should be noted. As we have seen, each term of the sum (48) corresponds to a polynomial of the sixth degree in k. However, expression (53) for $f_3$ is a polynomial of the fourth degree in k (the terms containing $k^6$ mutually cancel). A similar cancellation occurs with respect to the quantum number m (expression (53) does not contain a term $m^6$ even though each term in the summation (48) contains C raised to the third power and, by the same token, m raised to the sixth power).

## Fourth-Order Perturbation Theory

Let us present the general formula for the fourth-order correction to the energy according to perturbation theory:[22]

$$\begin{aligned}E_n^{(4)}=&\sum_i{}'\sum_j{}'\sum_k{}'\frac{V_{ni}V_{ij}V_{jk}V_{kn}}{(E_n^{(0)}-E_i^{(0)})(E_n^{(0)}-E_j^{(0)})(E_n^{(0)}-E_k^{(0)})}\\&-2V_{nn}\sum_i{}'\sum_j{}'\frac{V_{ni}V_{ij}V_{jn}}{(E_n^{(0)}-E_i^{(0)})^2(E_n^{(0)}-E_j^{(0)})}\\&+V_{nn}^2\sum_i{}'\frac{V_{ni}V_{in}}{(E_n^{(0)}-E_i^{(0)})^3}-E_n^{(2)}\sum_i{}'\frac{V_{ni}V_{in}}{(E_n^{(0)}-E_i^{(0)})^2}.\end{aligned} \tag{54}$$

From Eqs. (54) we obtain the following expression for $f_4$:

$$\begin{aligned}256f_4=&\sum_\mu{}'\sum_\nu{}'\sum_\sigma{}'\frac{(0|\mu)(\mu|\nu)(\nu|\sigma)(\sigma|0)}{(-\mu)(-\nu)(-\sigma)}\\&-2(0|0)\sum_\mu{}'\sum_\nu{}'\frac{(0|\mu)(\mu|\nu)(\nu|0)}{(-\mu)^2(-\nu)}\\&+(0|0)^2\sum_\mu{}'\frac{(0|\mu)(\mu|0)}{(-\mu)^3}-\sum_\mu{}'\frac{(0|\mu)^2}{(-\mu)}\sum_\nu{}'\frac{(0|\nu)^2}{(-\nu)^2},\end{aligned} \tag{55}$$

in deriving this expression we have used the fact that the quantum number k plays the role of the unperturbed energy, and we have also utilized formula (41) for the second-order correction.

Let us rewrite (55) in the following form:

$$\begin{aligned}256f_4=&\sum_\mu{}'\sum_\nu{}'\sum_\sigma{}'\frac{-1}{\mu\nu\sigma}(0|\mu)\{(\mu|\nu)(\nu|\sigma)-(0|0)\delta_{\mu,\nu}(\nu|\sigma)\\&-(\mu|\nu)(0|0)\delta_{\nu,\sigma}-(0|\nu)(\nu|0)\delta_{\mu,\sigma}+(0|0)^2\delta_{\mu,\nu}\delta_{\nu,\sigma}\}(\sigma|0),\end{aligned} \tag{56}$$

and in analogy with the two preceding approximations we now introduce the symbol

$$[\mu\nu\sigma], \tag{57}$$

which, just like its analogs (43) and (49), is the sum of two terms in (56) which differ by simultaneous changes in the signs of $\mu$, $\nu$, and $\sigma$. According to the same arguments which led us to formulas (46) and (51), we obtain the following expression for the symbol (57):

$$\begin{aligned}[\mu\nu\sigma]=2\cdot\text{the part of}\Big\{&-\frac{1}{\mu\nu\sigma}(0|\mu)((\mu|\nu)(\nu|\sigma)\\&-(0|0)\delta_{\mu,\nu}(\nu|\sigma)-(\mu|\nu)(0|0)\delta_{\nu,\sigma}-(0|\nu)(\nu|0)\delta_{\mu,\sigma}\\&+(0|0)^2\delta_{\mu,\nu}\delta_{\nu,\sigma})(\sigma|0)\Big\}.\quad\text{which is odd in k.}\end{aligned} \tag{58}$$

The expression appearing inside the curly brackets in (58) is a linear combination of products of four trinomials quadratic in k. Knowing the coefficients which appear in these trinomials, we can easily solve for expression (58). Thus, each symbol of the type defined by (57) and (58) is a certain odd polynomial of the seventh degree in k.

We note the following relations which the symbols (57) and (58) satisfy:

$$[\sigma\nu\mu]=[\mu\nu\sigma],\quad [-\mu-\nu-\sigma]=[\mu\nu\sigma],\quad [-\sigma-\nu-\mu]=[\mu\nu\sigma]. \tag{59}$$

An elementary scanning of the possible values of $\mu$, $\nu$, and $\sigma$ which are admitted by the properties of the matrix elements of $\xi^2$ indicates that (56) reduces to the sum of 21 symbols of the type defined by (57) and (58):

$$\begin{gathered}256f_4=[242]+[232]+[231]+[222]+[221]+[212]+[211]+[21-1]+\\ +[132]+[131]+[122]+[121]+[112]+[111]+[11-1]+[1-11]\\ [1-1-1]+[1-1-2]+[1-21]+[2-12]+[2-22].\end{gathered} \tag{60}$$

Here it turns out that

$$[2-22]\equiv0.$$

The following "identical" pairs occur among the remaining 20 symbols:

$$\begin{gathered}[132]=[231],\quad [122]=[221],\\ [112]=[211],\quad [1-1-2]=[21-1],\quad [1-1-1]=[11-1].\end{gathered} \tag{61}$$

(The relationships (61) are a direct consequence of (59). Thus, it is actually necessary to evaluate 15 expressions of the form (58). As a result of these (rather tedious!) calculations we obtain the following definitive expression for $f_4$:

$$\begin{gathered}f_4(k,|m|)={}^1/_{256}(-42756\,k^5+8910\,m^2k^3-46810\,k^3-{}^{909}/_4m^4k\\ +{}^{7389}/_2m^2k-{}^{22709}/_4\,k).\end{gathered} \tag{62}$$

It is necessary to note that, just as in the case of the case of the third-order correction, a partial cancellation of terms has occurred: The maximum power to which k and $|m|$ are raised in the individual terms of the sum (62) is equal to five whereas this power is equal to seven for the individual terms in expression (58).

From Eqs. (37), (40), (47), (53), and (62) we obtain the following expressions for $A_1$, $A_2$, $A_3$, and $A_4$:

$$\begin{gathered}A_1={}^3/_2(n_1-n_2)\equiv{}^3/_2q,\\ A_2={}^1/_{16}(-17\,n^2-51\,q^2+9\,m^2-19),\\ A_3={}^3/_{32}\,q(125\,n^2+125\,q^2-43\,m^2+153),\\ A_4={}^1/_{1024}(-10689\,n^4-53445\,q^4-106890\,n^2q^2-46810\,n^2-140430\,q^2\\ +8910\,n^2m^2+26730\,m^2q^2-22709+14778\,m^2-909\,m^4),\end{gathered} \tag{63}$$

where

$$q\equiv n_1-n_2 \tag{64}$$

denotes the so-called electric quantum number.[21] In the derivation of Eqs. (63) we have made substantial use of the two relationships

$$k_1+k_2=n,\quad k_1-k_2=n_1-n_2\equiv q. \tag{65}$$

Finally, by substituting expressions (63) into (38) and (39), we ultimately obtain

$$\begin{gathered}E=-\frac{1}{2n^2}+\frac{3}{2}nq\mathscr{E}+\frac{n^4}{16}(-17n^2+3q^2+9m^2-19)\mathscr{E}\\ +\frac{3}{32}n^7q(23n^2-q^2+11m^2+39)\mathscr{E}^3+\frac{n^{10}}{1024}(-5487n^4-147q^4+549m^4\\ -1806n^2q^2+3402n^2m^2+1134m^2q^2-35182n^2-5754q^2+8622m^2-16211)\mathscr{E}^4\end{gathered} \tag{66}$$

which is the formula for the energy of the hydrogen atom state with quantum numbers $n_1$, $n_2$, and m (or with quantum numbers n, m, and q) in an external, constant and homogeneous electric field, this formula being correct to terms of fourth order in $\mathscr{E}$ inclusively.

## 4. DISCUSSION OF THE RESULTS

Let us discuss the question of the agreement between expression (66) and the results of other calculations. The calculation up to and including the third-order correction is in complete agreement with previous results.[1-9,15,20,21] The remaining task is to compare the fourth-order correction from (66) with the analogous terms from the two earlier calculations in[9] and[15].

Let us begin with the comparison with Basu's result.[9] Since[9] was published in a journal which is almost inaccessible,1) we repeat Basu's formula here (in atomic units)

$$\begin{gathered}E^{(4)}_{\text{Basu}}=-\frac{n^{10}\mathscr{E}^4}{128}\{930n^4-525(m+1)n^3+(-231m^2+672m+5453)n^2\\ -(-210m^3-63m^2+1659m+1512)n+\\ +(-192m^4-210m^3+\underline{12840m^2}+1512m+\underline{3664)}+294n_1{}^2n_2{}^2-1050n^2n_1n_2\\ +294(m+1)nn_1n_2-(-420m^2+294m+3024)n_1n_2\},\\ m=|m|\geqslant0.\end{gathered} \tag{67}$$

As already mentioned, (67) contains arithmetic errors (the two terms which are underlined in (67) have incorrect coefficients). We have located the sources of the arithmetic errors in[9]. The separation constants found in[9] agree with the ones found above (if one changes from the quantum numbers $n_1$ and $n_2$, which were used in[9], to the quantum numbers $k_1$ and $k_2$). The mistake in[9] arose in connection with the solution for the formula analogous to the last expression in (39), in the term which corresponds to $({}^9/_2)A_2^2$ in our notation. On page 128 of[9], fifth line from the bottom, the number 1125 must be corrected to 1225, and 2601 $m^2$ must be changed to 4071 $m^2$. Taking this fact into consideration, the underlined terms in formula (67) should be corrected as follows: 3664 is changed to 2764, and 12840 $m^2$ is changed to $-390$ $m^2$. After insertion of the indicated corrections, formula (67) is identical to the corresponding term of Eq. (66). In order to verify this it is necessary to take account of the connection between $n_1$, $n_2$, and $m\equiv|m|$, and the principal quantum number n.

Now let us compare (66) with the result of the calculations by Bekenstein and Krieger.[15] Of the ten terms in (66) which contain the fourth-order correction, nine agree with the corresponding terms from[15]. However, instead of

$$-147\,q^4\equiv-147(n_1-n_2)^4$$

the term

$$3093(n_1-n_2)^4$$

is written down in[15]. It is difficult for us to judge the location of the source of this arithmetic error, since the intermediate calculations are not given in[15]. Nevertheless, we have verified that the expression obtained from the equation given in[15] for the separation constants agree with our results for these constants. Thus, there remains only one possible source of arithmetic error, namely the expanded expressions in (39). Thus, the assertion by Bekenstein and Krieger[15] that the quasiclassical approximation (more precisely, the improved Bohr-Sommerfeld quantization rule) and perturbation theory lead to identical results in the case of weak fields $\mathscr{E}$ is still valid (assuming, of course, that the coefficient of the term $(n_1 - n_2)^4$ is corrected).

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[1)] Bekenstein and Krieger [15] mention that they could not compare their results with those obtained by Basu. [9]

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