LETTER TO THE EDITOR

Perturbation theory within the O(4, 2) group for a hydrogen-like atom in the field of distant charge

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Abstract. In the O(4, 2) group an algebraic scheme of perturbation theory is proposed which enables one to find the energy and wavefunctions of bound states of a hydrogen-like atom in the field of the point charge placed at large distance R. It is shown that in each order of R^{-1} the correction to the wavefunction is expressed through a finite number of Coulomb functions of the discrete spectrum with a modified charge. Simple analytical expressions are obtained for the first and second corrections.

In recent years, many theoretical and experimental papers have been devoted to the behaviour of atoms in external electric and magnetic fields (Soloviev 1981, 1982, Braun 1983, Braun and Soloviev 1984, Clark *et al* 1984, Littman *et al* 1976, Zimmerman *et al* 1980). For a theoretical description of these systems one should first construct a perturbation theory for weak fields. However, the use of standard Rayleigh–Schrödinger perturbation theory leads to the appearance of infinite complex sums. Perturbation procedures have been proposed which enabled analytical expressions to be derived in some cases (Turbiner 1984).

Our approach is based on the dynamical O(4, 2) group of a hydrogen atom (Malkin and Man'ko 1965, 1966, Barut and Rasmussen 1973). As is known, the unitary irreducible representation of O(4, 2) algebra is related by the so-called tilting (scaling) transformation to the Coulomb functions of the discrete spectrum of the H atom while perturbations of the polynomial form are expressed through the generators of O(4, 2) algebra. Therefore, the calculation of corrections to eigenfunctions and eigenenergies is a pure algebraic procedure. Moreover the corrections to eigenfunctions are expressed through a limited number of basis functions of the representation.

We shall demonstrate the possibilities of our approach by examining a hydrogen-like atom in the field of a distant point charge. Though this problem has been investigated for many years (Krogdahl 1944, Coulson and Gillam 1947, Coulson and Robinson 1958, Power 1973, Komarov *et al* 1976), simple expansions for the wavefunctions were not obtained. Such expansions are necessary to formulate boundary conditions in the adiabatic representation of the three-body problem (Faifman *et al* 1976, Ponomarev *et al* 1981).

Let us recall some properties of the O(4, 2) group following papers by Bednar (1973) and Bechler (1977). The Lie algebra O(4, 2) is formed by 15 generators

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$(\alpha, \beta = 1, 2, \ldots, 6)$

$$L_{\alpha\beta} = -L_{\beta\alpha} \qquad [L_{\alpha\beta}, L_{\beta\gamma}] = \mathrm{i}g_{\alpha\alpha}L_{\beta\gamma} \tag{1}$$

where

$$g_{\alpha\alpha} = (1, 1, 1, 1, -1, -1).$$

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

$$
\begin{aligned}
L_{ij} &= x_i p_j - x_j p_i \equiv \varepsilon_{ijk} L_k \\
L_{i4} &= \tfrac{1}{2}(x_i \boldsymbol{p}^2 + 2\mathrm{i}p_i - 2\boldsymbol{x} \cdot \boldsymbol{p}p_i - x_i) \equiv A_i \\
L_{i5} &= \tfrac{1}{2}(x_i \boldsymbol{p}^2 + 2\mathrm{i}p_i - 2\boldsymbol{x} \cdot \boldsymbol{p}p_i + x_i) \\
L_{46} &= \tfrac{1}{2}(r\boldsymbol{p}^2 - r) \\
L_{56} &= \tfrac{1}{2}(r\boldsymbol{p}^2 + r) \\
L_{45} &= -\mathrm{i}(1 + \mathrm{i}\boldsymbol{x} \cdot \boldsymbol{p}) \\
L_{i6} &= -r p_i
\end{aligned}
\tag{2}
$$

where $p_k = -\mathrm{i}\partial/\partial x_k$, L_k and A_k are the momentum, moment and Runge–Lenz vector components, $r = (x_1^2 + x_2^2 + x_3^2)^{1/2}$.

Operators (1) and (2) act in the Hilbert function space with the scalar product

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

with respect to which they are self-conjugate. As a basis of the Hilbert space we choose eigenfunctions of three commuting operators L_{56}, A_3, L_3:

$$
\begin{aligned}
L_{56}|n_1 \bar{n}_2 m\rangle &= n|n_1 \bar{n}_2 m\rangle \\
A_3|n_1 \bar{n}_2 m\rangle &= (n_2 - n_1)|n_1 \bar{n}_2 m\rangle \\
L_3|n_1 \bar{n}_2 m\rangle &= m|n_1 \bar{n}_2 m\rangle.
\end{aligned}
\tag{4}
$$

The basis functions (4) in the parabolic coordinates

$$y_1 = r + x_3 \qquad y_2 = r - x_3 \qquad y_3 = \tan^{-1} x_2/x_1$$
$$\mathrm{d}^3 y = \tfrac{1}{4}(y_1 + y_2)\, \mathrm{d}y_1\, \mathrm{d}y_2\, \mathrm{d}y_3$$

have the form $(j = 1, 2)$

$$\Phi^{(0)}_{n_1 n_2 m}(y) = C_{n_1 n_2 m}\varphi_{n_1 m}(y_1)\varphi_{n_2 m}(y_2)(2\pi)^{-1/2}\, \mathrm{e}^{\mathrm{i}m y_3}
\begin{cases}
(-1)^m, & m > 0 \\
1, & m \leq 0
\end{cases}$$

$$C_{n_1 n_2 m} = 2^{1/2}\{n_1![(n_1 + |m|)!]^{-1} n_2![(n_2 + |m|)!]^{-1}\}^{1/2} \tag{5}$$

$$\varphi_{n_j m}(y_j) = [(n_j + |m|)!]^{-1} y_j^{|m|/2} \exp(-\tfrac{1}{2}y_j) L^{|m|}_{n_j + |m|}(y_j)$$

where $L^{|m|}_{n_j + |m|}(y_j)$ are the Laguerre polynomials (Courant and Hilbert 1953).

The functions (5) coincide in form with the Coulomb functions of the H atom and differ only by a factor $(-2E^{(0)})^{1/2}$ in the argument and the normalisation factor $C_{n_1 n_2 m}$ defined by condition (3). This fact simplifies considerably the construction of the procedure of perturbation theory on the basis of (4) and (5). However, it is more

convenient to use the unnormalised functions

$$|n_1 n_2 m\rangle = C_{n_1 n_2 m}^{-1} |n_1 \bar{n}_2 m\rangle \qquad (6)$$

since the operators L_{46} and L_{35} are defined on the functions (6) in the simplest way

$$L_{46}|n_1 n_2 m\rangle = \tfrac{1}{2}[(n_1 + |m|)|n_1 - 1 n_2 m\rangle + (n_1 + 1)|n_1 + 1 n_2 m\rangle$$
$$+ (n_2 + |m|)|n_1 n_2 - 1 m\rangle + (n_2 + 1)|n_1 n_2 + 1 m\rangle] \qquad (7)$$
$$L_{35}|n_1 n_2 m\rangle = \tfrac{1}{2}[-(n_1 + |m|)|n_1 - 1 n_2 m\rangle - (n_1 + 1)|n_1 + 1 n_2 m\rangle$$
$$+ (n_2 + |m|)|n_1 n_2 - 1 m\rangle + (n_2 + 1)|n_1 n_2 + 1 m\rangle].$$

Now let us apply the formalism of the $O(4, 2)$ group to the problem of the hydrogen-like atom in the charge field. Let the atom with the nuclear charge Z_a (atomic units are used throughout) be in the field of the charge Z_b placed at a distance R, which is larger than the size of the atom. Then the Schrödinger equation (axis x_3 is directed from Z_b to Z_a)

$$(\tfrac{1}{2}p^2 - Z_a/r - Z_b/|R + r| + Z_a Z_b/R - E)|\Psi\rangle = 0$$

takes the form

$$\left(\tfrac{1}{2}p^2 - Z_a/r - Z_b \sum_{k=1}^{\infty} R^{-k} r^{k-1}(-1)^{k-1} P_{k-1}(x_3/r) + Z_a Z_b/R - E\right)|\Psi\rangle = 0. \qquad (8)$$

We represent the solution (8) as the expansions

$$E = E^{(0)} + \sum_{k=1}^{\infty} R^{-k} E^{(k)} \qquad \Psi = \Psi_{n_1 n_2 m}^{(0)} + \sum_{k=1}^{\infty} R^{-k} \Psi^{(k)} \qquad (9)$$

where $E^{(0)} = -\tfrac{1}{2}(Z_a/n)^2$ and $\Psi_{n_1 n_2 m}^{(0)}$ are the energy and normalised wavefunction of a unperturbed problem, respectively. After multiplying (8) by r we have

$$\left(\tfrac{1}{2}r p^2 - Z_a - r E^{(0)} - \sum_{k=1}^{\infty} R^{-k} V^{(k)}(x_3, r)\right)|\Psi\rangle = 0 \qquad (10)$$

where

$$V^{(1)}(x_3, r) = E^{(1)} r - (Z_a - 1) Z_b r$$
$$V^{(k)}(x_3, r) = E^{(k)} r + Z_b r^k (-1)^{k-1} P_{k-1}(x_3/r) \qquad k \geq 2.$$

Further we perform the unitary transformation

$$\Phi = U\Psi = \exp(i\theta L_{45})\Psi$$
$$\tanh \theta = (1 + 2E^{(0)})/(1 - 2E^{(0)}) \qquad (11)$$

and use the relations $U^{-1}x_k U = (-2E^{(0)})^{1/2} x_k$, $r = L_{56} - L_{46}$, $x_3 = L_{35} - L_{34}$, $\tfrac{1}{2}r p^2 = \tfrac{1}{2}(L_{46} + L_{56})$. Then equation (10) becomes

$$\left(L_{56} - \frac{Z_a}{(-2E^{(0)})^{1/2}} - \frac{1}{(-2E^{(0)})^{1/2}} \sum_{k=1}^{\infty} R^{-k} V^{(k)}\left(\frac{L_{35} - L_{34}}{(-2E^{(0)})^{1/2}}, \frac{L_{56} - L_{46}}{(-2E^{(0)})^{1/2}}\right)\right)|\Phi\rangle = 0. \qquad (12)$$

Using for Φ the representation (9) and collecting in (12) terms at equal degrees of R,

we obtain the system of inhomogeneous equations ($k = 1, 2, \ldots$)

$$L(n)|\bar{\Phi}^{(0)}_{n_1 n_2 m}\rangle \equiv [L_{56} - Z_a/(-2E^{(0)})^{1/2}]|\bar{\Phi}^{(0)}_{n_1 n_2 m}\rangle = (L_{56} - n)|\Phi^{(0)}_{n_1 n_2 m}\rangle = 0$$

$$L(n)|\Phi^{(k)}\rangle = \frac{1}{(-2E^{(0)})^{1/2}}\left[V^{(k)}\left(\frac{L_{35} - L_{34}}{(-2E^{(0)})^{1/2}}, \frac{L_{56} - L_{46}}{(-2E^{(0)})^{1/2}}\right)|\bar{\Phi}^{(0)}_{n_1 n_2 m}\rangle \right.$$

$$\left. + \sum_{p=1}^{k-1} V^{(k-p)}\left(\frac{L_{35} - L_{34}}{(-2E^{(0)})^{1/2}}, \frac{L_{56} - L_{46}}{(-2E^{(0)})^{1/2}}\right)|\Phi^{(p)}\rangle \right]$$

$$\equiv f^{(k)}. \tag{13}$$

With relation (7) and the polynomial form of $V^{(k)}$ we expand the right-hand sides $f^{(k)}$ and corrections $\Phi^{(k)}$ over the states $|st\rangle = |n_1 + sn_2 + tm\rangle C_{n_1 n_2 m}$ which are normalised only in the case $s = t = 0$ (see (6)), i.e. $|00\rangle = \bar{\Phi}^{(0)}_{n_1 n_2 m}$

$$f^{(k)} = \sum_{s=-k}^{k} \sum_{t=-k}^{k} f^{(k)}_{st}|st\rangle = \frac{1}{(-2E^{(0)})^{1/2}}\left[V^{(k)}\left(\frac{L_{35} - L_{34}}{(-2E^{(0)})^{1/2}}, \frac{L_{56} - L_{46}}{(-2E^{(0)})^{1/2}}\right)|00\rangle \right.$$

$$+ \sum_{p=1}^{k} V^{(k-p)}\left(\frac{L_{35} - L_{34}}{(-2E^{(0)})^{1/2}}, \frac{L_{56} - L_{46}}{(-2E^{(0)})^{1/2}}\right)$$

$$\left. \times \left(\sum_{s=-p}^{p} a^{(p)}_{s-s}|s - s\rangle + \sum_{s=-p}^{p}\sum_{t=-p}^{p} b^{(p)}_{st}|st\rangle\right) \right]$$

$$\Phi^{(k)} = \sum_{s=-k}^{k} a^{(k)}_{s-s}|s - s\rangle + \sum_{s=-k}^{k}\sum_{t=-k}^{k} b^{(k)}_{st}|st\rangle \equiv \Phi^{(k)}(a) + \Phi^{(k)}(b).$$

The terms $\Phi^{(k)}(a)$ are due to the Coulomb degeneration in the layer $n = n_1 + n_2 + |m| + 1$ and form the zero-order function, which is independent of the magnitude of Z_b,

$$\Phi^{(0,k)}_{n_1 n_2 m} = \bar{\Phi}^{(0)}_{n_1 n_2 m} + \sum_{p=1}^{k} R^{-p}\Phi^{(p)}(a) \tag{14}$$

for the perturbation operator up to $(k + 2)$th order

$$V(k+2) = \sum_{p=1}^{k+2} R^{-p}V^{(p)}.$$

Taking into account the orthogonality of the functions $|st\rangle$ with weight r^{-1} according to (3) and $L(n)|st\rangle = (s + t)|st\rangle$ we rewrite the system of equations (13)

$$(s + t)b^{(k)}_{st}|st\rangle = f^{(k)}_{st}|st\rangle \qquad -k \leqslant s, t \leqslant k. \tag{15}$$

Equation (15) at $k = 1$, $s = t = 0$ becomes

$$f^{(1)}_{00}|00\rangle = (n/Z_a)^2[E^{(1)} - (Z_a - 1)Z_b](L_{56} - L_{46})|00\rangle$$

$$= (n/Z_a)^2[E^{(1)} - (Z_a - 1)Z_b]L_{56}|00\rangle$$

$$= (n/Z_a)^2[E^{(1)} - (Z_a - 1)Z_b]n|00\rangle = 0. \tag{16}$$

Hence we immediately obtain

$$E^{(1)} = (Z_a - 1)Z_b \qquad V^{(1)} \equiv 0 \qquad b^{(1)}_{st} = 0. \tag{17}$$

The calculation of corrections of a higher order also does not encounter any great difficulties. Indeed, taking into account (17) one can observe that $f^{(k)}_{st}$ depends linearly

on $E^{(p)}$, $1 \leq p \leq k$ and $a_{s-s}^{(l)}$, $b_{st}^{(l+1)}$, $1 \leq l \leq k-3$. This allows one to obtain the kth order correction to energy from the equation linear in $E^{(k)}$

$$f_{00}^{(k)} \equiv f_{00}^{(k)}(E^{(p)}, 1 \leq p \leq k, a_{s-s}^{(l)}, b_{st}^{(l+1)}, 1 \leq l \leq k-3) = 0. \tag{18}$$

Then we obtained

$$b_{st}^{(k)} = (s+t)^{-1} f_{st}^{(k)}(E^{(p)}, 1 \leq p \leq k, a_{s-s}^{(l)}, b_{st}^{(l)}, 1 \leq l \leq k-2). \tag{19}$$

Since $f_{s-s}^{(k+1)}$ is independent of $E^{(k+1)}$ we find $a_{s-s}^{(k-1)}$ from the equation

$$f_{s-s}^{(k+1)} = f_{s-s}^{(k+1)}(E^{(p)}, 1 \leq p \leq k, a_{s-s}^{(l)}, b_{st}^{(l)}, 1 \leq l \leq k-1) = 0. \tag{20}$$

Thus, in the $(k+1)$th order we first find $a_{s-s}^{(k-1)}$ and then $E^{(k+1)}$ and $b_{st}^{(k+1)}$. The calculation of the corrections by the linear equation (18)–(20) is reduced in each order to a pure algebraic procedure. Using the subroutine (18)–(20) up to the order R^{-4}, we obtain the wavefunctions up to order R^{-2}

$$a_{1-1}^{(1)} = -\tfrac{1}{2}(n/Z_a)(n_1+1)(n_2+|m|)$$

$$a_{1-1}^{(2)} = \tfrac{1}{2}(n/Z_a)^2(n_1+1)(n_2+|m|)(1+n_1-n_2)$$

$$a_{2-2}^{(2)} = \tfrac{1}{8}(n/Z_a)^2(n_1+1)(n_1+2)(n_2+|m|)(n_2+|m|-1)$$

$$b_{20}^{(2)} = -\tfrac{1}{8}(n/Z_a)^3 Z_b(n_1+1)(n_1+2) \tag{21}$$

$$b_{-20}^{(2)} = \tfrac{1}{8}(n/Z_a)^3 Z_b(n_1+|m|)(n_1+|m|-1)$$

$$b_{10}^{(2)} = \tfrac{1}{4}(n/Z_a)^3 Z_b[2(2n_1+2+|m|)-3(n_1-n_2)](n_1+1)$$

$$b_{-10}^{(2)} = -\tfrac{1}{4}(n/Z_a)^3 Z_b[2(2n_1+|m|)-3(n_1-n_2)](n_1+|m|).$$

The remaining seven coefficients are obtained up to the sign by interchanging n_1 by n_2

$$a_{-11}^{(1)} = -a_{1-1}^{(1)}(n_1 \leftrightarrow n_2), \qquad a_{-ss}^{(2)} = a_{s-s}^{(2)}(n_1 \leftrightarrow n_2), \qquad b_{os}^{(2)} = -b_{so}^{(2)}(n_1 \leftrightarrow n_2). \tag{22}$$

Applying the tilting operation $(Z_a^{1/2}/n) U^{-1}$ (equation (11)) to the calculated function $\Phi = \bar{\Phi}_{n_1 n_2 m}^{(0)} + R^{-1}\Phi^{(1)} + R^{-2}\Phi^{(2)}$ in accordance with Bednar (1973) and Bechler (1977) we have

$$\Psi = (Z_a^{1/2}/n) \exp(-i\theta L_{45})\Phi = \Psi_{n_1 n_2 m}^{(0)} + R^{-1} \sum_{s=-1}^{1} a_{s-s}^{(1)} \Psi_{n_1+sn_2-sm}^{(0)}$$

$$+ R^{-2} \sum_{s=-2}^{2} a_{s-s}^{(2)} \Psi_{n_1+sn_2-sm}^{(0)} + R^{-2} \sum_{s=-2}^{2} \sum_{t=-2}^{2} b_{st}^{(2)} \Psi_{n_1+sn_2+tm}^{(0)} \tag{23}$$

where

$$\Psi_{n_1+sn_2+tm}^{(0)}\left(\frac{Z_a}{n}y\right)$$

$$= \frac{Z_a^{3/2}}{n^2} C_{n_1 n_2 m} \varphi_{n_1+sm}\left(\frac{Z_a}{n}y_1\right) \varphi_{n_2+tm}\left(\frac{Z_a}{n}y_2\right) \frac{e^{imy_3}}{(2\pi)^{1/2}} \begin{cases} (-1)^m, & m > 0 \\ 1, & m \leq 0 \end{cases}$$

in the notation of (5). Note that $\Psi_{n_1+sn_2+tm}^{(0)}$ coincide up to the normalisation factor with the parabolic functions of the Coulomb problem with the new charge $Z_* = Z_a n_*/n$ and with the new principal quantum number $n_* = n + s + t$ (see equation (9)).

Now we normalise the function (23) up to the terms R^{-2}

$$\Psi_{\text{norm}} = \Psi^{(0)}_{n_1 n_2 m}\left[1 - R^{-2}\left(\sum_{s=-2}^{2}\sum_{t=-2}^{2} b^{(2)}_{st}(\Psi^{(0)}_{n_1 n_2 m}|\Psi^{(0)}_{n_1+sn_2+tm})\right.\right.$$

$$+\tfrac{1}{2}(a^{(1)}_{1-1}C_{n_1 n_2 m}/C_{n_1+1n_2-1m})^2 + \tfrac{1}{2}(a^{(1)}_{-11}C_{n_1 n_2 m}/C_{n_1-1n_2+1m})^2\Big)\Big]$$

$$+R^{-1}\sum_{s=-1}^{1} a^{(1)}_{s-s}\Psi^{(0)}_{n_1+sn_2-sm}$$

$$+R^{-2}\left(\sum_{s=-2}^{2} a^{(2)}_{s-s}\Psi^{(0)}_{n_1+sn_2-sm} + \sum_{s=-2}^{2}\sum_{t=-2}^{2} b^{(2)}_{st}\Psi^{(0)}_{n_1+sn_2+tm}\right). \qquad (24)$$

The orthogonality condition in (24)

$$(\Psi^{(0)}_{n_1 n_2 m}|\Psi^{(0)}_{n_1+sn_2+tm}) = \int d^3 y \, \Psi^{*(0)}_{n_1 n_2 m}\left(\frac{Z_a}{n}y\right)\Psi^{(0)}_{n_1+sn_2+tm}\left(\frac{Z_*}{n_*}y\right)$$

$$= n^{-1}\langle n_1 n_2 m|L_{56} - L_{46}|n_1+sn_2+tm\rangle = \delta_{so}\delta_{to}$$

is fulfilled only at $Z_* = Z_a$, i.e. at $s + t = 0$.

Taking into account that $E^{(2)} = \tfrac{3}{2}(n/Z_a)Z_b(n_1 - n_2)$ and

$$\sum_{s=-2}^{2}\sum_{t=-2}^{2} b^{(2)}_{st}(\Psi^{(0)}_{n_1 n_2 m}|\Psi^{(0)}_{n_1+sn_2+tm}) = -\tfrac{1}{2}(n/Z_a)^2 E^{(2)}$$

we finally obtain

$$\Psi_{\text{norm}} = \Psi^{(0)}_{n_1 n_2 m}\{1 - \tfrac{1}{8}(n/Z_a)^2 R^{-2}[(n_1+1)(n_2+|m|)(n_1+|m|+1)n_2$$

$$+ n_1(n_2+1)(n_1+|m|)(n_2+|m|+1)]\} + R^{-1}\sum_{s=-1} a^{(1)}_{s-s}\Psi^{(0)}_{n_1+sn_2-sm}$$

$$+R^{-2}\sum_{s=-2}^{2} a^{(2)}_{s-s}\Psi^{(0)}_{n_1+sn_2-sm} + R^{-2}$$

$$\times\left(\sum_{s=-2}^{2}\sum_{t=-2}^{2} b^{(2)}_{st}\Psi^{(0)}_{n_1+sn_2+tm} + \tfrac{1}{2}(n/Z_a)^2 E^{(2)}\Psi^{(0)}_{n_1 n_2 m}\right). \qquad (25)$$

It should be noted that the last term in (25) corresponds to the Stark correction to the hydrogen-like wavefunction

$$R^{-2}\left(\sum_{s=-2}^{2}\sum_{t=-2}^{2} b^{(2)}_{st}\Psi^{(0)}_{n_1+sn_2+tm} + \tfrac{1}{2}(n/Z_a)^2 E^{(2)}\Psi^{(0)}_{n_1 n_2 m}\right)$$

$$= \frac{Z_b}{R^2}\sum_{n\neq n'} \frac{(\Psi^{(0)}_{n_1 n_2 m}|x_3|\Psi^{(0)}_{n'_1 n'_2 m})}{E^{(0)}_n - E^{(0)}_{n'}}\Psi^{(0)}_{n'_1 n'_2 m}$$

which is linear with respect to the electric field Z_b/R^2. The remaining terms define the zero-order wavefunction for the quadrupole and octupole interactions.

Thus, we have shown that an explicit use of the dynamical $O(4, 2)$ group of the Coulomb problem allows one to obtain the simple expansions (21), (22) and (25) in powers of R^{-1} for a hydrogen-like atom in the point charge field. In this case only the zero-order corrections (14) contain the Coulomb functions of the unperturbed atom with fixed principal quantum number n. In contrast with the ordinary procedure of the Rayleigh-Schrödinger perturbation theory the remaining corrections are expressed through a finite number of modified Coulomb functions corresponding to a changed

charge Z_* of the nucleus of the atom. The method suggested can be used in the theory of the hydrogen-like atom for any perturbation of the polynomial form.

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