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Quantum Geometry : New numerical approach to quantization of the quasistationary states of Dirac-Slater equation

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Abstract An advanced procedure for quantization of the quasistationary states of the relativistic Dirac-Slater equation is developed within a gauge-invariant relativistic many-body perturbation theory ([1], [2]). New numerical approach to calculating spectra of the quantum (atomic) systems with an account of relativistic and exchange-correlation corrections is proposed. The special procedure is realized in order to to obtain high-accuracy eigen values and wave function by an iterative procedure, checking the number of node to insure convergence toward the right eigenvalue.

Keywords Dirac-Slater equation · Quasistationary states · Eigen functions and eigen values of energy

Mathematics Subject Classification (2000) 55R05 · 53B05

1 Introduction

The problems of calculating the eigen values and eigen functions of the the different quantum operators is relating to a number of the most important and actual problems of the modern quantum geometry and quantum theory of the many-body systems. In this paper we have developed an advanced procedure for quantization of the quasistationary states of the relativistic Dirac-Slater equation within gauge-invariant relativistic many-body perturbation theory ([1], [2]). The sufficiently full reviews of the modern methods for calculating the eigen values of energies and eigen functions for different operators (Hamiltonians) of the finite

quantum (atomic) systems are presented in a number of recent monographes and books (see, for example,[1], [3], [4], [6], [7]) and references therein)). Let us remind that the well-known multi-configuration Dirac-Fock (MCDF) method (in the versions of the Desclaux program, Dirac package etc, see for example, [3], [5], [6]) is the most reliable version of calculation for multielectron systems with a large nuclear charge; in these calculations one- and two-particle relativistic effects are taken into account practically precisely. The calculation program of Desclaux is compiled with proper account of the finiteness of the nucleus size. However, a detailed description of the role of the nucleus size and its influence for quite heavy atomic systems requires the further investigation. I In our paper a new numerical approach to calculating spectra of the eigen values for the finite quantum (atomic) systems with an account of relativistic, exchange-correlation corrections is proposed. The wave functions zeroth approximation basis is found from the Dirac-Slater equations solution. The potential includes the self-consistent mean field potential, the electric of a nucleus (within the Fermi model). The special procedure is realized in order to to obtain high-accuracy eigen values and wave function by an iterative procedure, checking the number of node to insure convergence toward the right eigenvalue. In an advanced Dirac-Slater approach in order to conserve a consistence one should take into account the inter-electron correlation corrections, for example, by means using the technique of the correlation potentials of the Slater type ([1], [4]). New element of the approach is connected with using ab initio consistent quantum electrodynamics approach to construction of the optimal one-quasiparticle representation in the Dirac-Slater approach. Numerical estimates are given for the eigen values of energies (the transition energies) in a number of the lithium-like multicharged ions with the different value od the nuclear charge Z.

2 Dirac-Slater equation: quantization of the quasistationary states

In this section we describe the key moments of our approach to quantization of the quasistationary (stationary) states of the relativistic Dirac-Slater equation with an account of relativistic, exchange-correlation effects in the Slater and correlation potential approximation.

One-particle wave functions are found from solution of the relativistic Dirac equation, which can be written in the central field in a two-component form (see,

for example,([1], [7]):

$$\frac{\partial F}{\partial r} + (1+\chi)\frac{F}{r} - (\epsilon + m - v)G = 0,$$
$$\frac{\partial G}{\partial r} + (1-\chi)\frac{G}{r} - (\epsilon - m - v)F = 0. \quad (1)$$

Here we put the fine structure constant $\alpha = 1$. The moment number

$$\chi = \begin{cases} -(1+1), & j > 1 \\ 1, & J < 1 \end{cases} \quad (2)$$

The potential v includes the self-consistent mean field potential, the electric potential of a nucleus and the Slater exchange and effective correlation potentials (see, for example,([1], [4])).

At large χ the radial functions F and G vary rapidly at the origin of coordinates:

$$F(r), G(r) \approx r^{\gamma - 1}, \quad (3)$$
$$\gamma = \sqrt{\chi^2 - \alpha^2 Z^2}.$$

This involves difficulties in numerical integration of the equations in the region $r \to 0$. To prevent the integration step becoming too small it is convenient to turn to new functions isolating the main power dependence: $f = Fr^{1-|\chi|}$, $g = Gr^{1-|\chi|}$. The Dirac equation for F and G components are transformed as:

$$f' = -(\chi + |\chi|)\frac{f}{r} - \alpha Z V g - \left(\alpha Z E_{n\chi} + \frac{2}{\alpha Z}\right) g,$$
$$g' = (\chi - |\chi|)\frac{g}{r} - \alpha Z V f + \alpha Z E_{n\chi} f. \quad (4)$$

Here the Coulomb units (C.u.) are used; The system of Eq. (4) has two fundamental, solutions. We are interested in the solution regular at $r \to 0$. The boundary values of the correct solution are found by the first term s of the expansion into the Taylor series:

$$g = \frac{(V(0) - E_{n\chi}) r \alpha Z}{2\chi + 1}; \qquad f = 1 \quad \text{at} \quad \chi < 0,$$
$$f = \left(V(0) - E_{n\chi} - \frac{2}{\alpha^2 Z^2}\right) \alpha Z; \qquad g = 1 \quad \text{at} \quad \chi > 0. \quad (5)$$

The condition $f, g \to 0$ at $r \to \infty$ determines the quantified energies of the state $E_{n\chi}$. At correctly determined energy $E_{n\chi}$ of the asymptotic f and g at $r \to \infty$ are:

$$f, g \sim \exp\left(-r/n^*\right), \quad (6)$$

where $n^* = \sqrt{\frac{1}{2|E_{n=\chi}|}}$ is the effective main quantum number. The Eq.(4) was solved by the Runge-Kutt method (see details in ([1], [7]).

3 Nuclear potential of Dirac-Slater equation: The Gauss-model differential equations method

Earlier ([1]-[10]) the different characteristics of the heavy hydrogen-like, Ne-like and other ions with the nucleus in the form of a uniformly charged sphere have been calculated. Here the smooth Gaussian function of the charge distribution in the nucleus is used. Using the smooth distribution function (instead of the discontinuous one) simplifies the calculation procedure and permits flexible simulation of the real distribution of the charge in the nucleus. As in refs.([1], [7]) one could set the charge distribution in the nucleus $\rho(r)$ by the Gaussian function. With regard to normalization we have:

$$\begin{aligned} \rho(r|R) &= \frac{4\gamma^{3/2}}{\sqrt{\pi}}\exp(-\gamma r^2); \\ \int_0^\infty drr^2\rho(r|R) &= 1; \\ \int_0^\infty drr^3\rho(r|R) &= R, \end{aligned} \tag{7}$$

where $\gamma = frac4\pi R^2$, R is the effective nucleus radius. The following simple dependence of R on Z assumed:

$$R = 1.60 \cdot 10^{-13} Z^{1/3} \quad \text{(cm)}. \tag{8}$$

Such definition of R is rather conventional. We assume it as some zeroth approximation. Further the derivatives of various characteristics on R are calculated. They describe the interaction of the nucleus with outer electron; this permits recalculation of results, when R varies within reasonable limits. The Coulomb potential for the spherically symmetric density $\rho(r|R)$ is:

$$V_{\text{nucl}}(r|R) = -\frac{1}{r}\int_0^r dr'r'^2\rho(r'|R) + \int_r^\infty dr'r'^2\rho(r'|R). \tag{9}$$

It is determined by the following system of differential equations ([1], [7]):

$$\begin{aligned} V_{\text{nucl}}(r,R) = \frac{1}{r^2}\int_0^r dr'r'^2\rho(r',R) \equiv \frac{1}{r^2}y(r,R); \\ y'(r,R) = r^2\rho(r,R); \\ \rho'(r,R) = -8\gamma^{5/2}\frac{r}{\sqrt{\pi}}\exp(-\gamma r^2) = -2\gamma r\rho(r,R) = -\frac{8r}{\pi r^2}\rho(r,R) \end{aligned} \tag{10}$$

with the boundary conditions:

$$V_{\text{nucl}}(r,0) = -\frac{4}{\pi r};$$
$$y(0,R) = 0; \tag{11}$$
$$\rho(0,R) = \frac{4\gamma^{3/2}}{\sqrt{\pi}} = \frac{32}{R^3}.$$

4 The Dirac-Slater equation for the three-body atomic system

Consider the Dirac-Slater type equations for a three-electron system $1s^2$nlj. Formally they fall into one-electron Dirac-Slater equations for the orbitals 1s1s and nlj with the potential:

$$V(r) = 2V(r|1s) + V(r|1nlj) + V_{\text{ex}}(r) + V(r|R). \tag{12}$$

$V(r|R)$ includes the electrical nuclear potential and the exchange-correlation potentials; the components of the Hartree potential:

$$V(r|i) = \frac{1}{Z}\int d\overrightarrow{r}' \frac{\rho(r|i)}{|\overrightarrow{r} - \overrightarrow{r}'|}, \tag{13}$$

where $\rho(r|i)$ is the distribution of the electron density in the state $|i\rangle$, V_{ex} is the (Slater type)potential of the exchange inter-electron interaction plus the correlation potential of the Gunnarsson-Lundqvist type (see details in [1]). The main exchange effect will be taken into account if in the equation for the 1s orbital we assume

$$V(r) = V(r|1s) + V(r|nlj) \tag{14}$$

and in the equation for the nlj orbital

$$V(r) = 2V(r|1s). \tag{15}$$

The rest of the exchange and correlation effects will be taken into account in the first two orders of the PT by the total inter-electron interaction ([1], [7]).

The used expression for $\rho(r|1s)$ coincides with the precise one for a one-electron relativistic atom with a point nucleus. The finiteness of the nucleus and the presence of the second 1s electron are included effectively into the energy E_{1s}. Actually, for determination of the properties of the outer nlj electron one iteration is sufficient. Refinement resulting from second iteration (by evaluations) does not exceed correlation corrections of the higher orders omitted in the present calculation. The relativistic potential of core (the 'screening' potential) $2V^{(1)}(r|1s) = V_{\text{scr}}$ has correct asymptotic at zero and in the infinity; at $\alpha \to 0$ it

Table 1 Results calculation of the nuclear finite size correction into energy ($cm^{\smile 1}$) of the low transitions for Li-like ions and values of the effective radius of nucleus ($10^{\smile 13}$ cm)

Z	$2s_{1/2}$-$2p_{1/2}$	$2s_{1/2}$-$2p_{3/2}$	R
20	−14.9	−15.3	3.26
30	−117.1	−117.7	3.73
41	−658.6	−669.7	4.14
59	−6609.1	−6844.0	4.68
69	−20688.2	−21710.1	4.93
79	−62312.5	−66929.6	5.15
92	−267320.4	−288307.8	5.42

changes to an appropriate potential constructed on the basis of non-relativistic hydrogen-like functions.

As example in Table 1 the results of our calculation of the nuclear correction into eigen values of energy (energies of the low transitions) for Li-like ions are presented. The calculation showed also that a variation of the nuclear radius on several percents could lead to changing the energies values on dozens of thousands 10^3 cm^{-1}. We also note that naturally our numerical data differ from the analogous, practically exact data in ([7]). Surely the authors of ([7]) have used more exact and more consistent method, however even sufficiently simplified model of the Dirac-Slater type allows getting mathematically reasonable results. However, at whole these questions in more detailed considerations should be studied in a separate paper.

5 Conclusions

In conclusion let us underline that we have proposed a new procedure for quantization of the stationary and quasistationary states of the relativistic Dirac-Slater type equation within using a formalism of the gauge-invariant relativistic many-body perturbation theory ([1], [7]). We have elaborated a new numerical approach to calculating spectra of the quantum (atomic) systems with an account of relativistic and exchange-correlation corrections, which is based on the differential equations method by Glushkov-Ivanov [2]. The special procedure is realized in order to to obtain high-accuracy eigen values and wave function by an iterative procedure, checking the number of node to insure convergence toward the right eigenvalue. The illustrative numerical estimates on the nuclear finite size correction into eigen values of energy for the low transitions in the spectra of some Li-like ions are presented and sufficiently well agreed with the available quite exact data.

References

1. Glushkov, A. : Relativistic quantum theory. Quantum mechanics of atomic systems – Odessa, Astroprint (2008), 700p.
2. Glushkov, A., Ivanov, L.: Radiation decay of atomic states: Atomic residue and gauge non-invariant contributions – Phys. Lett.A., **170** (1992), P.33-37.
3. Grant, I.: Relativistic Quantum Theory of Atoms and Molecules –Oxford (2008), 650p.
4. Slater, J.: Methods of self-consistent field in theory of atoms, molecules and solids – Wiley, McHill (1972), 780p.
5. Parpia, F., Froese-Fischer, C., Grant, I.: Generalized relativistic atomic structure package: GRASP – Comp.Phys.Commun., **94** (1996), P.249-270.
6. Safronova, U., Safronova, M.: Third-order relativistic many-body calculations of energies, transition rates, hyperfine constants, and blackbody radiation shift – Phys. Rev. A., **79** (2009), P.022512.
7. Glushkov, A., Khetselius, O., Florko, T. et al : Gauge-invariant QED perturbation theory approach to calculating nuclear electric quadrupole moments, hyperfine structure constants – Frontiers in Quantum Systems in Chemistry and Physics. Berlin, Springer, **18** (2008), P.504-522.
8. Glushkov, A., Khetselius, O., Sukharev, D. et al : Relativistic quantum theory of heavy ions and hadronic atomic systems: Spectra and energy shifts – Theory and Applications of Comput.Chem., (2009), P.131-136.
9. Khetselius, Yu.: Relativistic perturbation theory calculation of the hyperfine structure parameters for some heavy-element isotopes – Int. Journ. of Quantum Chem., **109** (2009) P.3330-3335.
10. Florko, T.: Theoretical determination of the radiative transition probabilities in spectra of Ne-like multicharged ions. – Photoelectronics, **19** (2010) P.51-55.

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