Materials of Conferences

CORRELATION ENERGY OF DOUBLY EXCITED STATES OF HELIUM-LIKE ATOMS

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1. Selection and description of used approach

Main problem at calculation of multielectron atoms, which elementary case are helium-like atoms, eventually is the necessity to take into account of interaction between electrons. The review of approximate methods of the solution of this problem (as of 2000 year) it is possible to find in [1].

In the present work we use the one-configuration first approximation of a variational method (further VM_1), in which one parameter - charge of the nucleus varies only, and all interaction of electrons is with each other reduced only to mutual shielding by them of this charge. Thus VM_1 is most simple from all possible methods, which use approximation of independent particles. The description VM_1 can be found in many sources (for example - in [2]) and there is no necessity to consider it here in full details.

We note, that we not take into account in this approach exchange effects. The wave function of two-electron atom in this approximation is look as

$$\psi = \psi_1 \cdot \psi_2 , \quad (1)$$

where ψ_1 and ψ_2 - wave functions of separate electrons, which differ from hydrogen-like functions only by replacement in them of a real charge of the nucleus Z on effective charges Z_{e1} and Z_{e2}, which are variational parameters.

Eventually formula of energy (hereinafter everywhere in the text as units of energy is used Rydberg -Ry) two-electron atom calculated by the method VM_1 is noted as

$$E_{He1} = \varepsilon_1 \cdot (Z_{e1}/n_1)^2 + \varepsilon_2 \cdot (Z_{e2}/n_2)^2 , \quad (2)$$

where n_1 and n_2 - general quantum numbers of appropriate electrons, and ε_1 and ε_2 - factors, which take into account relativistic effects and influence of the nucleus. In the present work we have taken their value from experiment under the formula

$$\varepsilon = E_{H\,exp} \cdot (n/Z)^2 , \quad (3)$$

where $E_{H\,exp}$ - experimental value of energy of hydrogen-like atom for given Z and given n.

2. Correlation energy

The residual between precision energy of atom and energy calculated by one from methods of approximation of independent particles is named as correlation energy.

We can estimate accuracy of approach VM_1 with the help of correlation energy. In the present work we have analyzed of correlation energy of a method VM_1 for nl_1nl_2 states of helium-like atoms, where n - main quantum number, common for both electrons, and l_1 and l_2 - orbital quantum numbers of appropriate electrons. The similar analysis for a ground state of two-electron atoms can be found in various sources (for example in [2]), but we could not find any publication of similar investigation for doubly excited states (DES) and we claim for superiority in this problem. We have analyzed of correlation energy for all nl_1nl_2 states of He-like atoms, for which it was possible to find the experimental data now, but because of limitation of the size of the article we shall present here as an example only data obtained for nsns(1S) states. The values E_{He1}, calculated by a method VM_1, values of energy $E_{He\,exp}$, taken from experiment, and also value of correlation energy $E_{cor} = E_{He\,exp} - E_{He1}$, for nsns (1S) states are given in a table 1.

We have analyzed relation of correlation energy from Z and n, and have detected, that the nl_1nl_2 states are divided into two groups. The first group involves lowest states for the given configuration, i.e. states with least possible n. It is states, in which at least one electron is on the such orbit, for which n = l + 1. In the old quantum theory this condition corresponds to the special case of circular orbits. Second group involves all remaining states of configurations, i.e. states with n > l + 1 for everyone from two electrons. We obtained the formulas

$$E_{cor} = (1/2) \cdot C \cdot (1/n) \cdot Z \cdot [\, k_1 - k_2 \cdot (Z-1)/Z \,] \quad (4)$$

and

$$E_{cor} = (1/2) \cdot C \cdot (1/n) \cdot Z \cdot k_1 \quad (5)$$

accordingly for the first and second group of states, where k_1 and k_2 - integer factors, which values are given in a table 2, and C - numerical factor. The values C, at which formula (4) and (5) give precision coincidence with experiment, are given in a table 1 for nsns (1S) states. It is easy to see, that C with a large degree of probability is a constant and is in range 0,110-0,116, i.e. is close to 1/9.

Table 1. The data of experiment and calculations for nsns (1S) states of helium-like atoms for n from 1 up to 3

State	Z	$E_{He\ exp}$ (Ry)	E_{He1} (Ry)	E_{cor} (Ry)	C	E_{He} (Ry)	Ref. $E_{He\ exp}$
1s1s (1S)	1	1,0550	0,9448	0,1101	0,110	1,0559	[3]
	2	5,8068	5,6948	0,1120	0,112	5,8059	[4]
	3	14,5597	14,4457	0,1140	0,114	14,5568	[4]
	4	27,3131	27,1987	0,1143	0,114	27,3099	[4]
	5	44,0699	43,9561	0,1137	0,114	44,0672	[4]
	6	64,8318	64,7202	0,1116	0,112	64,8313	[4]
	7	89,6035	89,4946	0,1089	0,109	89,6057	[4]
	8	118,3845	118,2829	0,1016	0,102	118,3940	[4]
	9	151,1885	151,0900	0,0985	0,099	151,2011	[4]
	10	188,0111	187,9201	0,0910	0,091	188,0312	[4]
2s2s (1S)	1	0,2972	0,2444	0,0528	0,106	0,2999	[5]
	2	1,5571	1,4436	0,1135	0,114	1,5547	[6]
	3	3,8077	3,6431	0,1646	0,110	3,8098	[7]
	4	7,0788	6,8434	0,2354	0,118	7,0656	[7]
	5	11,3354	11,0452	0,2902	0,116	11,3229	[8]
3s3s (1S)	2	0,7206	0,6431	0,0776	0,116	0,7171	[9]
	6	7,4304	7,2260	0,2044	0,102	7,4482	[10]
	7	10,2379	9,9849	0,2530	0,108	10,2442	[11]
	8	13,4581	13,1900	0,2681	0,101	13,4863	[10]

Table 2. Factors k1 and k2

State	k_1	k_2
nsns(1S)	2	*2*
npnp(1D)	2	*2*
nsnp(3P)	2	*0*
npnp(3P)	1	*0*
nsnp(1P)	1	*3*
npnp(1S)	*0*	*4*

Finally we have following semi-empirical formula for calculation of full energy of helium-like atom for nl_1nl_2 states

$$E_{He} = E_{He1} + E_{cor}, \quad (6)$$

where E_{He1} is calculated by a method VM_1 and follows from the formula (2), and E_{cor} follows from the formulas (4) and (5) and is entered because of analysis of the experimental data.

In that specific case of states nsns (1S), npnp (1D), ndnd (1G) etc., when both electrons are on same orbit, or, as speak, occupy the same quantum cell, the formulas (4) and (5) receive especially simple kind

$$E_{cor} = C\cdot(1/n) \quad (7)$$

for $n = l + 1$ and

$$E_{cor} = C\cdot(1/n)\cdot Z \quad (8)$$

for $n > l + 1$.

We note, that our refusal to take into account of exchange degeneration is justified for these states from any point of view.

The particular case of the formula (7) for n = 1 corresponds to a ground state of helium-like atoms (1s1s) and results to E_{cor} = C, i.e. the correlation energy in this case does not depend from Z and it was marked by Bethe as the curious fact in [2]. The Hartree-Fock method also results in independence of correlation energy of a nuclear charge in case of a ground state 1s1s , but the constant obtained at it, has average value 0,085 unlike 0,111 for case of a method VM_1. The correlation energy of a Hartree-Fock method was a theme of many works at the end of 1950s and at the beginning of 1960s, however after appearance of the first experimental data on DES of atoms in a middle of 1960s the point of view has prevailed, that the Hartree-Fock method and generally approximation of independent particles is inapplicable for the description of a similar class of states because of large increase for them of correlation energy. The obtained above formulas show, that at least in case of a method VM_1 the approximation of independent particles can be applied successful for DES if to consider correlation energy not as an annoying error, but as the simply taken into account correction with interesting physical properties which will be discussed below. Moreover, simplicity of obtained expressions results that the correlation energy is transformed from a problem into a proof of effectiveness of approximation of independent particles. Already now it is possible to use algorithm of calculation , offered us, as the simple and at the same time rather precision semi-empirical approximation to describe known lines of spectra of helium-like atoms and to predict or to help to identify until now unknowns lines.

The data of calculation of energy E_{He} under the formula (6), in the supposition, that C = 1/9, are given in table1 for those of nsns (1S) states, for which the experimental data are known . Goodness of fit of calculations with experiment quite satisfactory, taking into account errors of measurements and approximations at calculations. The data of the same calculation for a unknown for today nsns (1S) states at n from 4 up to 10 and Z from 1 up to 10 are given as an example in a table 3.

Table 3. The data of calculation for nsns (1S) states of helium-like atoms for n from 4 up to 10

Z	E_{He}(Ry)	E_{He}(Ry)	E_{He}(Ry)	E_{He}(Ry)	E_{He}(Ry)	E_{He}(Ry)	E_{He}(Ry)
	4s4s	**5s5s**	**6s6s**	**7s7s**	**8s8s**	**9s9s**	**10s10s**
1	0,0893	0,0616	0,0459	0,0360	0,0293	0,0245	0,0210
2	0,4175	0,2762	0,1980	0,1500	0,1183	0,0962	0,0802
3	0,9958	0,6508	0,4612	0,3457	0,2699	0,2174	0,1794
4	1,8242	1,1854	0,8356	0,6230	0,4839	0,3879	0,3186
5	2,9029	1,8802	1,3212	0,9820	0,7605	0,6078	0,4979
6	4,2319	2,7352	1,9180	1,4227	1,0997	0,8771	0,7170
7	5,8114	3,7504	2,6260	1,9452	1,5014	1,1959	0,9763
8	7,6417	4,9261	3,4455	2,5494	1,9657	1,5641	1,2758
9	9,7230	6,2623	4,3763	3,2355	2,4927	1,9818	1,6152
10	12,0556	7,7592	5,4183	4,0035	3,0823	2,4490	1,9943

3. Results

3.1. From a point of view of physics of the formula (4) and (5) result to exotic, i.e. in nonclassical relation of energy of interaction of charged particles to a distance between them.

If in the formulas, obtained by us, to present n as a radius of atom r (remembering, that in hydrogen-like atoms $r \sim n^2$), we shall receive for different parts of full energy of atom of relation

$$E \sim 1/r^k ,$$

where for terms, calculated by the method VM_1, k = 1, that completely corresponds to the classical law of the Coulomb, and for correlation energy, k = 1/2. Thus here there is an additional interaction decreasing on a distance slower, than Coulomb force.

The additional calculations, carried out by us, have shown, that the relation $E \sim 1/r^{1/2}$, or accordingly $E \sim 1/n$, occurs only in that case, when both electrons have identical general quantum numbers n. We found proofs of existence of similar relation of correlation energy from a general quantum number of external electrons not only in helium-like atoms, but also in atoms with large number of electrons, and in molecules and crystals.

That fact, that coincidence of general quantum numbers n at both electrons is required for appearance of relation $E \sim 1/n$, can indicate resonant character of additional interaction. Moreover it results in electron-electron attraction, instead of repulsion and very strongly depends on a configuration of spin and orbital moment, that makes it even less similar to electrostatic

interaction, but similar to interaction, which exist between protons in the nucleus.

3.2. From a mathematical point of view it is obvious, that if in two-electron atom there were no nonclassical interactions, the method VM_1 would give precisiouly analytical solution of a three-body problem. The simplicity of the formulas (4-8) allows to hope, that the analytical solution is possible and with taking into account of nonclassical interactions. It would become possible after an evaluation of correlation energy E_{cor} and constant C from certain general principles.

3.3. From a practical point of view it is interesting, that since some value n usual Coulomb repulsion electrons (decreasing as $1/n^2$) will become less additional not - Coulomb attractions (decreasing as 1/n). It can result in macroscopic case to join of electrons in certain stable or metastable structures - quasineutral (if number of electrons equally to number of positive ions) or charged, just as the protons are integrated in the charged nucleus. The similar processes could spontaneously happen in strong rarefied plasma of intersidereal space, in high layers of an ionosphere of the Sun, Earth and other cases, in which the large distances between charged particles (appropriate to the large values n) are realized. It is possible, that the similar effects could explain at least some from anomalous plasma-like effects observed in atmosphere and an ionosphere, such as a ball lightning etc.

To receive a similar new states of substance in experiment, it is necessary, that the electrons of substance were excited synchronously, i.e. had identical energy and identical values n in each instant . To the present moment not much of similar (doubly exited) states is obtained even for two-electron atoms . For molecules them it is known even less. Moreover both in case of atoms, and in case of molecules the values n are not reached yet value, at which the attraction between electrons exceeds a repulsion between them. In case of macroscopic skew fields the problem of synchronous excitation of electrons up to maximum large n till now not to pose, though technically it is not unattainable, since the similar problems are decided at creation of quantum generators of coherent electromagnetic radiation.

Let's remind also, that the explanation of a superconductivity involves appearance of additional electron-electron attraction , which exceeds Coulomb repulsion under certain conditions.

Moreover there are the direct analogies between additional correlation energy of electrons in superconductors and additional correlation energy of electrons in separate atoms in the literature (see for example [3]), and the Cooper pair sometimes is represented as two electrons moving round an induced positive charge, and is compared to atom of a helium.

All of this makes probablis bose-einstein condensation of synchronously excited electrons both in atoms, and in macroscopic skew fields from that moment, when not - Coulomb attraction of electrons will begin to exceed Coulomb repulsion. The similar superconductivity already could be named super-high-temperature.

Conclusion

The approach based on separation of full energy of multielectron systems on classical Coulomb and nonclassical not - Coulomb parts, allows on the one hand to simplify calculations, and with another - to see interesting regularities, which were not visible at use of more complex methods. Most interesting is the discovery of that fact, that under certain conditions electron-electron attraction exceeds electron-electron repulsion. The most important practical consequence it is the capability of existence of ordered structures of a new type in the special way exited substance.

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POLYMER-IMPREGNATED CONCRETE BASED ON WATER DISPERSION OF VINYL CHLORIDE

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For the purpose of defining maximal chemical durability of the formed material at the optimal con-