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RELATIVISTIC EFFECTS IN THREE-ELECTRON ATOMS*

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Hartree–Fock and Dirac–Fock energies have been calculated from numerical functions for the configurations $1s^2ns$ ($n = 2,3$), $1s^2np$ ($n = 2,3,4$), $1s^23d$, $1s2s^2$ and $1s2p^2$ of the atoms Li I through C IV. The resulting relativistic corrections are compared with existing results of the perturbational treatment.

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1. *Introduction*

Atoms belonging to the lithium isoelectronic series are of a special interest from both theoretical and experimental points of view. Very accurate solutions of the Schrödinger equation for three-electron atoms are now available [1–5]. In order to compare results of these calculations with experimental data, accurate values of the relativistic corrections are necessary.

The most rigorous way of estimating the relativistic corrections is offered by the Dirac–Hartree–Fock (DHF) method with perturbational inclusion of the Breit term [6, 7]. The DHF method was recently applied by several authors to evaluate the spectroscopic properties of the lithium-like atoms [8, 9]. In particular, Armstrong et al. [8] performed a detailed study of the relativistic effects on the probabilities of $2s \rightarrow 2p$, $2s \rightarrow 3p$ and $2p \rightarrow 3d$ transitions. An influence of the Breit interaction on the fine structure intervals in the $1s2p^2$ ^4P and $1s2s2p$ $^4P^0$ states was investigated by Cheng et al. [9].

The relativistic corrections to the energies of $1s^2nl$ configurations, calculated as the first-order perturbation to the Hartree–Fock (HF) energies, were published a few years ago [10]. The purpose of the present research is to carry out a systematic study of the relativistic corrections tothe energies of $1s^2nl$ and $1snl^2$ configurations in the framework of the DHF method. The relativistic wavefunctions have been obtained in numerical form using a DHF program developed by Desclaux [7]. Numerical solutions of the HF equations obtained by means of the Froese–Fischer program [11] have been used as the nonrelativistic references.

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2. *Results and discussion*

The total DHF energies of the configurations under consideration are collected in Table I. The Breit corrections are included as the first order perturbation. In all the cases the average energy of a configuration rather than the energy of a specific state was subject to the minimization procedure. The average energy of a configuration in the relativistic case is defined as follows:

TABLE I

Average Dirac–Hartree–Fock energies (in hartrees) of configurations

Configuration	Li I	Be II	B III	C IV
$1s_{1/2}^2\ 2s_{1/2}$	-7.433270	-14.279525	-23.381897	-34.739383
$1s_{1/2}^2\ 2p_{1/2}$	-7.365602	-14.132909	-23.159379	-34.442660
$1s_{1/2}^2\ 2p_{3/2}$	-7.365601	-14.132885	-23.159239	-34.442204
$1s_{1/2}^2\ 3s_{1/2}$	-7.310748	-13.879855	-22.563706	-33.362688
$1s_{1/2}^2\ 3p_{1/2}$	-7.293721	-13.841766	-22.504948	-33.283490
$1s_{1/2}^2\ 3p_{1/2}$	-7.293720	-13.841758	-22.504906	-33.283356
$1s_{1/2}^2\ 3d_{3/2}$	-7.292509	-13.835632	-22.492017	-33.262924
$1s_{1/2}^2\ 3d_{5/2}$	-7.292509	-13.835629	-22.492004	-33.262883
$1s_{1/2}^2\ 4p_{3/2}$	-7.268729	-13.741000	-22.278640	-32.882481
$1s_{1/2}^2\ 4p_{3/2}$	-7.268729	-13.740997	-22.278622	-32.882423
$1s_{1/2}\ 2s_{1/2}^2$	-5.344798	-10.042580	-16.244757	-23.950992
$1s_{1/2}\ 2p_{1/2}\ 2p_{3/2}$	-5.205457	-9.806631	-15.912915	-23.523392
$1s_{1/2}\ 2p_{3/2}^2$	-5.200810	-9.798895	-15.901950	-23.508907
$1s_{1/2}\ 2p_{1/2}^2$	-5.191677	-9.783927	-15.881521	-23.483638

$$E_{\mathrm{Av}}^{\mathrm{DHF}} = \sum_J (2J+1)E_J^{\mathrm{DHF}} / \sum_J (2J+1), \tag{1}$$

where J is the total angular momentum quantum number, E_J^{DHF} is the DHF energy of a given state and the sums are extended over all the states arising from the given configuration in *jj* coupling. In the cases of configurations with one electron outside a closed shell, in our case $1s_{1/2}^2(nl)_j$ and $1s_{1/2}2s_{1/2}^2$, the sums in (1) reduce to a single term and $E_{\mathrm{Av}} = E_J$.

The experimental ("exact") energy of an atom in a given state may be expressed in the following way:

$$E^{\mathrm{exact}} = E^{\mathrm{HF}} + E^{\mathrm{rel}} + E^{\mathrm{corr}} + E^{\mathrm{n}} + E^{\mathrm{r}}, \tag{2}$$

where E^{HF} is the Hartree–Fock energy, $E^{\mathrm{rel}} = E^{\mathrm{DHF}} - E^{\mathrm{HF}}$, E^{corr} is the correction resulting from the electron correlation, E^{n} — corrections due to finite mass and size of the nucleus and E^{r} — the radiative corrections. The most important contributions to (2) are E^{corr} and E^{rel}.

For all the configurations under consideration the HF equations [11] have been solved. The relativistic corrections E^{rel} have been obtained as differences between $E_{\mathrm{Av}}^{\mathrm{DHF}}$ and $E_{\mathrm{Av}}^{\mathrm{HF}}$ calculated for the same configuration in *jj* coupling. The relativistic corrections to the

TABLE II

Relativistic and correlation corrections (in μhartrees) to the average energies of configurations

Configuration	Li I		Be II		B III		C IV	
	E^{rel}	E^{corr}	E^{rel}	E^{corr}	E^{rel}	E^{corr}	E^{rel}	E^{corr}
$1s_{1/2}^2\ 2s_{1/2}$	−544	−45341	−2130	−47412	−5906	−48745	−13322	−49682
$1s_{1/2}^2\ 2p_{1/2}$	−532	−45087	−2049	−48470	−5660	−50705	−12778	−52125
$1s_{1/2}^2\ 2p_{3/2}$	−532		−2025		−5520		−12322	
$1s_{1/2}^2\ 3s_{1/2}$	−535	−43887	−2064	−45010	−5657	−45739	−12656	−46241
$1s_{1/2}^2\ 3p_{1/2}$	−532	−43964	−2042	−45425	−5592	−46347	−12514	−46937
$1s_{1/2}^2\ 3p_{3/2}$	−532		−2035		−5551		−12379	
$1s_{1/2}^2\ 3d_{3/2}$	−532	−43546	−2039	−44461	−5564	−45093	−12410	−45536
$1s_{1/2}^2\ 3d_{5/2}$	−532		−2037		−5551		−12369	
$1s_{1/2}^2\ 4p_{1/2}$	−533	−43693	−2039	−44742	−5568	−45395	−12427	−45816
$1s_{1/2}^2\ 4p_{3/2}$	−533		−2036		−5550		−12370	
$1s_{1/2}\ 2s_{1/2}^2$	−609		−2077		−5337		−11550	
$1s_{1/2}\ 2p_{1/2}2p_{3/2}$	−552		−1804		−4556		−9718	
$1s_{1/2}\ 2p_{3/2}^2$	−533		−1698		−4195		−8797	
$1s_{1/2}\ 2p_{1/2}^2$	−565		−1896		−4883		−10566	

average energies of configurations are given in Table II. For comparison corrections E^{corr} for $1s^2nl$ configurations are also given. The values of E^{corr} have been obtained as differences between the exact eigenvalues of the nonrelativistic Hamiltonian corresponding to a point and infinite mass nucleus (estimated in Ref. [12]) and the HF energies. A small correction due to an influence of the relativistic effects to E^{corr} has been neglected. One can see that the relative importance of E^{rel} grows up very fast along the series. For Li I the value of E^{rel} is only about 1.2% of the value of E^{corr}, for Be II — 4.5%, for B III — 11%–12% and for C IV — 24%–27%. It is interesting to note that in the case of Li I the values of $|E^{\mathrm{rel}}|$ for $1s2s^2$ and $1s2p^2$ configurations are larger than for the ground state configuration $1s^22s$. However the dependence on the nuclear charge of the corrections is weaker in the case of $1s2s^2$ and $1s2p^2$ than in the case of $1s^2nl$ configurations and already for Be II the relativistic correction to the ground state energy is the largest one. Only in the case of Li I the value of $|E^{\mathrm{corr}}|$ for the ground state is larger than for any other $1s^2nl$ configuration. For ionized atoms the correlation energy for $1s^22p$ configuration is the largest one (compare also [10]).

In order to complete the description of the corrections to the energy levels, Table III presents relativistic and correlation corrections to the energy differences between the centers of gravity of excited configurations and the ground state configuration. For comparison the relativistic corrections obtained as the first order perturbation to the HF energies [10] are also given. One can see that, except for $1s^22p$ configuration, the results of the DHF and perturbational calculations are very close (for a more detailed discussion see Ref. [13]).

TABLE III

Relativistic (ΔE^{rel}) and correlation (ΔE^{corr}) corrections (in μhartrees) to excitation energies of the centers of gravity of configurations

Configuration	Li I			Be II			B III			C IV		
	ΔE^{rel}		ΔE^{corr}	ΔE^{rel}		ΔE^{corr}	ΔE^{rel}		ΔE^{corr}	ΔE^{rel}		ΔE^{corr}
	HFP[a]	DHF[b]		HFP[a]	DHF[b]		HFP[a]	DHF[b]		HFP[a]	DHF[b]	
$1s^22p$	4	12	254	87	97	−1058	355	339	−1960	943	848	−2443
$1s^23s$	4	9	1454	64	66	2402	255	249	3006	670	664	3441
$1s^23p$	8	12	1377	91	93	1987	350	342	2398	934	898	2745
$1s^23d$	9	12	1795	91	92	2951	355	350	3652	961	937	4146
$1s^24p$	8	11	1648	96	93	2670	360	349	3350	952	933	3866
$1s2s^2$		−65			53			569			1772	
$1s2p^2$		−1			362			1473			3916	

[a] First order perturbation correction to HF energy (Ref. [10]).

[b] This work.

As results from the data presented in Table III, the contributions of the relativistic corrections to the excitation energies in the case of Li I constitute only 1%–5% of the contributions due to the electron correlation effects. However the relative contributions of the relativistic effects grow up very fast with the nuclear charge and already for C IV they reach 20%–35% of the correlation corrections.

A comparison between experimental, perturbational HF, and DHF fine structure splittings of ^2P levels is given in Table IV. It is interesting to note that in most cases the perturbational treatment gives better agreement with experiment than the DHF procedure.

TABLE IV

Fine structure splittings of doublet levels (in μhartrees)

Configuration	Be II			B III			C IV		
	Exp[a]	HFP[d]	DHF[e]	Exp[b]	HFP[d]	DHF[e]	Exp[c]	HFP[d]	DHF[e]
$1s^22p$	30	27	25	155	144	140	491	472	456
$1s^23p$	9	7	7	46	41	41	144	137	135
$1s^23d$	3	1	3	13	11	13	48	46	42
$1s^24p$	4	0	3	19	21	18	60	55	42

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