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# Failure of relativistic codes in the non-relativistic limit: the role of Brillouin configurations

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In the present letter we solve a long standing problem with relativistic calculations done with the widely used Multi-Configuration Dirac-Fock Method. We show, using Relativistic Many-Body Perturbation Theory (RMBPT), how even for relatively high- $Z$ , relaxation or correlation causes the non-relativistic limit of states of different total angular momentum but identical orbital angular momentum to have different energies. We identify the role of single excitations obeying to Brillouin's theorem in this problem. We show that with large scale calculations in which this problem is properly treated, we can reproduce very accurately recent high-precision measurements in F-like Ar, and turn then into precise test of QED

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Relativistic atomic structure codes, mostly Multi-Configuration Dirac-Fock (MCDF) packages, are now of widespread use in many sectors of physics, and the need for reliable, relativistic calculations is stronger than ever (see, e.g., [1] for examples in Astrophysics). However, the difficulties of doing reliable calculations are numerous, and still largely underestimated. For example a puzzle that was noted already twenty-two years ago [2] has received little attention, and has never been solved, although it may lead even in very simple calculation to wrong energy values. In Ref. [2] it was shown that relativistic self-consistent field procedures do not produce, in a number of cases, the correct non-relativistic limit of zero fine structure splitting when the speed of light is tuned to infinity. Ref. [2] suggested explicit calculation of this *non-relativistic offset* and subsequent correction of the relativistic result as a remedy, although no justification for the procedure was provided. Here we will penetrate the origin of the non-relativistic shift using the tools of perturbation theory and advanced MCDF calculations. We use these tools to show the role of relaxation in the N.R. offset, and prove that the inclusion of specific mono-excitations in the MCDF basis removes it. We also provide justification to the subtraction procedure.

We will concentrate on the fine-structure splitting in a F-like ion which was used as a model system already in Ref. [2] as accurate measurements have been performed very recently [3]. With high experimental accuracy, even for  $Z = 18$ , it is important to be aware of this problem which seriously affects the comparison with experiment on the present day level. Reference [3] does not discuss this issue and it is thus unknown if the theoretic

cal calculations performed there account for this problem. We will further present accurate calculations of the fine structure splitting in F-like argon both with Relativistic Many-Body Perturbation Theory (RMBPT) and with the Multi-Configuration Dirac-Fock (MCDF) method. It is shown that by comparison with accurate experimental results [3] it is possible to test the calculations on self-energy and other radiative corrections in a true many-electron surrounding.

With RMBPT the fine-structure splitting in a F-like system is calculated as the binding energy difference between the  $2p_{1/2}$  and  $2p_{3/2}$  electron in the corresponding Ne-like system. The lowest order approximation of this binding energy is the negative of the orbital energy of the removed electron in the Hartree-Fock approximation. The remaining electrons are at this stage considered as *frozen* in their orbitals in spite of the removal of one electron. The most important correction to this first approximation is then the *relaxation* of the electrons due to the presence of the hole. The term *relaxation* usually denotes the correction found by a single configuration restricted Hartree-Fock (or *Dirac-Fock* in the relativistic case) calculation in the presence of the hole. The non-relativistic shift has its origin already at this level and we will now concentrate on this shift and postpone the discussion of higher order corrections.

To analyze the relaxation contribution with perturbation theory it is natural to start from the closed shell system and systematically correct for the removal of one electron. Two properties characterize a specific perturbation expansion contribution; one is the order of the perturbation and the other is the number of excitations.

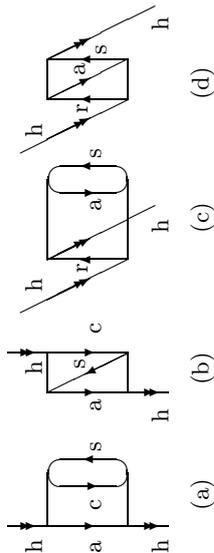


FIG. 1: Illustration of the contributions entering in second order perturbation theory. Diagrams(a-b) show single excitations and diagrams (c-d) double excitations (correlation). Downgoing single arrows denote core orbitals, downgoing double arrows denote the hole and upgoing arrows denote excited orbitals.

Fig. 1 shows the contributions entering in second order perturbation theory. Fig. 1(a-b) show single excitations and Fig. 1(c-d) double excitations. The *relaxation*, i.e., the effects included by a single configuration Hartree-Fock calculation in perturbation theory part of the single excitations; the ones that preserve the one-particle angular symmetry of the orbital being excited.

From now on we specialize the discussion on systems with one (non- $s$ ) electron removed from a closed core like F-like ions. In lowest order of the perturbation expansion the correction of this type to the wavefunction for orbital  $b$  is

$$\rho_b^{relax}(\ell_s = \ell_b, j_s = j_b) = - \sum_s^{exc} \frac{\langle s | \{ \{ h s \} | V_{12} | \{ h b \} \rangle}{\varepsilon_b - \varepsilon_s} \quad (1)$$

where  $h$  denote the removed electron, the curly brackets antisymmetrization and the minus sign is due to the removal of  $h$ .  $V_{12}$  is the two-electron interaction, e.g., the Coulomb interaction. The energy corrections are then calculated as

$$\sum_b^{core} \langle \{ b h \} | V_{12} | \{ \rho_b^{relax} h \} \rangle \quad (2)$$

In this way all types of diagrams in Fig. 1 (a-b) with either orbital  $a = h$  or  $c = h$  and  $\ell_s = \ell_b$ ,  $j_s = j_b$  are included, i.e., the single excitations that preserve the

angular structure. It can be noted that the single excitation contributions form a class of diagrams that can be summed until convergence in an iterative scheme, see, e.g., Refs. [4, 5]. Here we will not pursue this line, however, since our purpose is to analyze the relaxation in the non-relativistic limit and show why a state with a hole in  $n\ell_{j=\ell-1/2}$  and one with a hole  $n\ell_{j=\ell+1/2}$  do not reach the same energy in this limit. For this it is sufficient to study relaxation in second order.

As an example, take diagram Fig. 1(a) with orbital  $a = h$  and  $\ell_s = \ell_b$ , a typical relaxation contribution. The orbitals used to evaluate the diagram are solved using the Hartree-Fock potential from the closed shell core and the radial part of the  $2p_{1/2}$  and the  $2p_{3/2}$  orbital will be identical when we let  $c \rightarrow \infty$ . The problem comes instead from the spin-angular part. Since

$$| \ell m_\ell s m_s \rangle = \sum_{j m_j} | (\ell s) j m_j \rangle \langle (\ell s) j m_j | \ell m_\ell s m_s \rangle \quad (3)$$

decoupling of spin and orbital angular momentum cannot be done without summing over all total angular momenta,  $j$ . An unambiguous way to see how this influences our example of Fig. 1(a) with orbital  $a = h$  and  $\ell_s = \ell_b$  is to compare the angular contribution non-relativistically and relativistically. The electron-electron interaction is expressed as

$$\frac{1}{r_{12}} = \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} \mathbf{C}^k(1) \cdot \mathbf{C}^k(2), \quad (4)$$

where  $k$  denotes the rank of the spherical tensor operator  $\mathbf{C}$ , which works on the orbital part of wavefunctions. Non relativistically the angular part can be evaluated as

$$\sum_b^{core} \sum_k 2 \frac{1}{2k+1} \frac{1}{2\ell_h+1} \langle \ell_h || \mathbf{C}^k || \ell_h \rangle^2 \langle \ell_b || \mathbf{C}^k || \ell_b \rangle^2. \quad (5)$$

This is in fact identical to the following expression in the coupled space where two extra sums appear over intermediate total angular momenta

$$\sum_b^{core} \sum_k \sum_{j_h}^{\ell_h \pm \frac{1}{2}} \sum_{j_b}^{\ell_b \pm \frac{1}{2}} \frac{1}{2k+1} \frac{1}{2j_h+1} \langle j_h || \mathbf{C}^k || j_h \rangle^2 \langle j_b || \mathbf{C}^k || j_b \rangle^2, \quad (6)$$

That these two expressions give the same result can be understood by standard angular momentum algebra techniques.

In a restricted Dirac-Fock calculation there will be no sums over intermediate angular momenta. Instead only  $j_h = j_{h'}$  is allowed, i.e., the hole is not allowed to fluctuate to the other fine structure component, and  $j_{b'} = j_b$  is required, i.e., the corrections to orbital  $b$  do not change its angular structure. The spin-angular part used is thus

$$\sum_b^{core} \sum_k \frac{1}{2k+1} \frac{1}{2j_h+1} \langle j_h || \mathbf{C}^k || j_h \rangle^2 \langle j_b || \mathbf{C}^k || j_b \rangle^2, \quad (7)$$

TABLE I: Summary of the contributions. All calculations use the 2002 values for fundamental constants [6, 7] (eV). Experimental values are from wavelength provided in Ref. [3] converted to vacuum values using [8]

	$2p_{1/2}$	$2p_{3/2}$	$\Delta$
Contributions			
Ne-like DF orb. ener.	426.50002	424.13211	2.36791
$\Delta$ DF-Breit	-0.22659	-0.13576	-0.09083
h.o. retardation	-0.00011	0.00079	-0.00090
QED corr.	0.01353	0.00755	0.00598
Contributions specific to RMBPT			
2nd order core-core, Coul	-4.48509	-4.42587	-0.05921
core-core, Breit	-0.01187	-0.00814	-0.00373
correlation, Coul	2.56726	2.55763	0.00962
correlation, Breit	0.02391	0.02018	0.00373
h.o. contr. (Coul.+Breit)	0.16559	0.15885	0.00674
$\Delta$ DF Breit orbitals	0.00198	0.00043	0.00156
Total (RMBPT)	424.54863	422.30777	2.24086
Experiment			2.24010
Contributions specific to MCDF			
Relaxation (Coul)	-3.10800	-3.05931	-0.04869
Relaxation (Breit)	-0.00406	-0.00314	-0.00092
Correlation (Coul $\rightarrow$ $5g$ )	1.42466	1.39604	0.02862
Correlation (Breit $\rightarrow$ $5g$ )	-0.01359	0.00741	-0.02100
Total (MCDF)	424.58585	422.34569	2.24016
Experiment			2.24010

which will clearly not produce the same result as Eq. 5, and which further cannot give identical results for e.g.,  $j_h = 1/2$  and  $j_h = 3/2$ , which is easily seen from the  $k = 2$  contribution which is zero for  $j_h = 1/2$ , but not for  $j_h = 3/2$ . The difference can also be readily demonstrated numerically for a system as F-like neon where the second order contribution to the relaxation gives an unphysical fine structure offset of 0.024 eV in the  $c \rightarrow \infty$  limit. Following the recipe from Ref. [2] and correcting the result calculated with the true value of  $c$  with this offset, we obtain a relaxation contribution to the fine structure splitting of  $-0.058$  eV. After iteration of the relaxation contributions the corrected value reaches  $\sim -0.050$ , in line with the Coulomb relaxation contribution of  $\sim -0.049$ , listed in Table I. This value has been corrected using the same procedure. The small difference is probably due to small differences in the classification of relaxation and correlation contributions.

The lesson here is that since the summation over all possible couplings of spin and orbital angular momenta of the intermediate states are necessary to reproduce the uncoupled situation a correct non-relativistic limit cannot be achieved with any single configuration self consistent field calculation. In other words, still for the system under consideration, one has to include more than one

configuration relativistically to reproduce the single configuration non-relativistic result in a relativistic framework.

With several configurations included it should in principle be possible to reach the correct non-relativistic limit, in practice one can, however, generally not achieve this in a *truncated* calculation. In practice the number of configurations has to be truncated for all but the smallest systems. It is common for example, to restrict the calculation to double excitations from the dominating configuration, but just as double excitations are needed to be added to the single excitations to obtain the correct non-relativistic limit, triple excitations will be needed to be added to corresponding double excitations. One has to be careful in considering the meaning of single and double excitation. For example the  $1s^2 2s^2 2p^4 3p$  is a single excitation in the  $LS$  coupling sense. Yet in  $jj$  coupling it gives rise to 5 configurations in the  $J = 1/2$  case, two of which are double excitations in the  $jj$  sense ( $2p_{1/2} 2p_{3/2}^4 \rightarrow 2p_{1/2}^2 2p_{3/2}^2 3p_{1/2}$  and  $2p_{1/2}^2 2p_{3/2}^2 3p_{3/2}$ ). With many-body perturbation theory it is natural to start the calculation of the binding energy of the  $2p_j$  electron with the closed shell Ne-like system defining the zeroth order Hamiltonian. The perturbation, the full interaction with the removed electron, will then be relatively large and it is definitely necessary to go beyond second order to obtain good results even for a relatively heavy system as F-like argon. On the other hand the zeroth order Hamiltonian has a correct non-relativistic limit by construction and it is easy to control the excitations included during the perturbation expansion. The MCDF method effectively calculates the bulk of the electron-electron interaction, but the price to pay is a wrong non-relativistic limit. An unsolved question was whether or not inclusion of a large amount of correlation can alleviate this problem and reduce the offset. In the present work we have added to the original configuration all single and double excitations up to a given maximum  $n$  and  $\ell$ . We went from  $3d$  to  $5g$  for the case with a normal speed of light, and up to  $6h$  for the non-relativistic limit. This represents respectively 299, 1569, 4339 and 9127 fully relaxed  $jj$  configurations for the  $J = 1/2$  case, and 456, 2541, 7356 and 15915 for the  $J = 3/2$ .

The calculations are repeated with different lists of configurations. In one group of calculations, we include all single and double excitation in the  $jj$  sense, except for the single excitations, that should have a contribution only in the third order, as stated by Brillouin's theorem [9, 10, 11]. Again we use here this theorem in the  $jj$  sense, i.e., we exclude all configurations transformed from the initial one by replacing an orbital with quantum numbers  $n, \kappa$  by one with  $n', \kappa$ , where  $\kappa$  is the Dirac angular number. In a second group we include all single and double excitations. In both groups, we do calculations once with only the Coulomb interaction be-

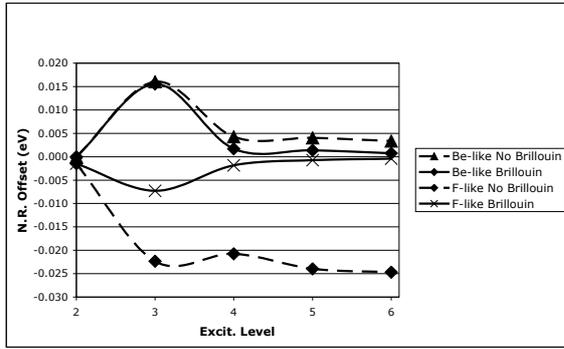


FIG. 2: Comparison of the non-relativistic offset evaluated with or without configurations obeying Brillouin's theorem for Be-like and F-like argon

tween electrons used in the evaluation of wavefunctions and energies, and once with the full Breit interaction in the evaluation of wavefunctions and mixing coefficients. This allows to include high-orders of the Breit interaction in the calculation. In each group the Coulomb only calculation is done also a second time with a large value for the speed of light. The evolution of the N.R. shift as a function of the maximum excitation used in the MCDF process is plotted on Fig. 2, for both F-like and Be-like ions, to show the generality of what is observed: the N.R. offset tends to a non-zero constant value when Brillouin configurations are excluded, and to zero when all single excitations are included.

The different contributions to the MCDF result, and the variation of the correlation energy and non-relativistic offset with and without Brillouin configurations are presented in Table II. When comparing both results, it is clear that subtracting the N.R. offset and excluding Brillouin single excitations, or including Brillouin single excitations lead to the same result. The agreement with experiment and RMBPT results is excellent in both cases, even though the quality of the convergence when including Brillouin single excitations is not as good as in the other case. It should also be noted that the evaluation of the radiative corrections, the self-energy screening (SES) with the help of the Welton approximation [12] leads to a very good agreement with experiment.

In conclusion we have proven, by comparing RMBPT and MCDF results, that the N.R. offset is due to relax-

ation and should go away when doing a complete calculation. We then showed that in the MCDF case, the offset is going to zero if a large enough configuration space is used, but only if Brillouin configurations are included. In practice subtracting the N.R. offset and excluding Brillouin single excitations lead to the same value, but numerical convergence of the self-consistent field process is much easier in the former case. Finally, failing to account for the N.R. offset leads to poor results, even at a moderately large  $Z$ , a fact that does not seem to have received enough attention in many MCDF calculations.

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TABLE II: Contributions to the MCDF energy affected by the N.R. offset (eV). “ $\Delta E$  doub. Exc.  $\rightarrow n = i$ ”: correlation energy for the configuration space which include all double excitations up to principal quantum number  $n = i$ . Rel. Val. : Relativistic Value. N.R. Off.: Offset obtained at the non-relativistic limit.

	Rel. Val.	N.R. Off.	Diff.
Dirac-Fock Coulomb	2.31626	-0.00148	2.31774
Brillouin single excitations excluded			
$\Delta E$ Exc. $\rightarrow n = 3$	-0.01855	-0.02086	0.00231
$\Delta E$ Exc. $\rightarrow n = 4$	-0.01421	-0.01926	0.00505
$\Delta E$ Exc. $\rightarrow n = 5$	-0.01641	-0.02247	0.00606
Total	2.21621	-0.02395	2.24016
Diff. With Exp.	-0.02389		0.00006
All single and double excitations included			
$\Delta E$ Exc. $\rightarrow n = 3$	-0.00371	-0.00582	0.00211
$\Delta E$ Exc. $\rightarrow n = 4$	0.00445	-0.00037	0.00482
$\Delta E$ Exc. $\rightarrow n = 5$	0.00661	0.00075	0.00586
Total (S.E.S. Welton)	2.23923	-0.00073	2.23996
Diff. With Exp.	-0.00087		-0.00014