Nonrelativistic Limit of Dirac-Fock Codes: The Role of Brillouin Configurations

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We solve a long standing problem with relativistic calculations done with the widely used multiconfiguration Dirac-Fock method. We show, using relativistic many-body perturbation theory (RMBPT), how, even for relatively high-Z, relaxation or correlation causes the nonrelativistic limit of states of different total angular momentum but identical orbital angular momentum to have different energies. We show that only large scale calculations that include all single excitations, even those obeying Brillouin's theorem, have the correct limit. We reproduce very accurately recent high-precision measurements in F-like Ar, and turn then to a precise test of QED. We obtain the correct nonrelativistic limit not only for fine structure but also for level energies and show that RMBPT calculations are not immune to this problem.

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Relativistic atomic structure codes, mostly multiconfiguration 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 22 years ago [2] has never been solved, although even in very simple calculations it may lead 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 nonrelativistic (N.R.) limit of zero for the fine-structure splitting (FSS) when the speed of light is tuned to infinity. As a remedy, Ref. [2] suggested explicit calculation of this *nonrelativistic offset* and subsequent subtraction of it from the relativistic result, although no justification for the procedure was provided. Moreover, this paper said nothing on how to correct individual energy levels. Here we will penetrate the origin of the nonrelativistic 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 monoexcitations in the MCDF basis removes it. We also provide justification to the subtraction procedure and show that not only the FSS needs to be corrected, but also the level energy, e.g., when transitions between different shells are studied. It is also worth noting that this problem appears in the optimized level scheme when each level energy and wave function is optimized separately. This scheme is used only when the highest accuracy for correlation is required. Often the average level (AL) scheme is used, in which the *same* J-average wave function is used to calculate the energy of all FS components. In the AL scheme the N.R. offset does not appear, but the accuracy is much lower.

We will concentrate on the ground state configuration of an F-like ion that 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. 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 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 an F-like system is calculated as the binding energy difference between the $2p_{1/2}$ and the $2p_{3/2}$ 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 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 nonrelativistic 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 for a one-hole state with perturbation theory, it is natural to start from the closed shell system and systematically correct for the removal of one electron. Figure 1 shows the contributions entering in second order. Figures 1(a) and 1(b) show fluctuations to two holes and one excited orbital and Figs. 1(c) and 1(d) true double excitations. The relaxation, i.e., the effects included by a single configuration restricted Hartree-Fock calculation, is in perturbation theory part of Figs. 1(a) and 1(b); the ones where the hole is not fluctuat-

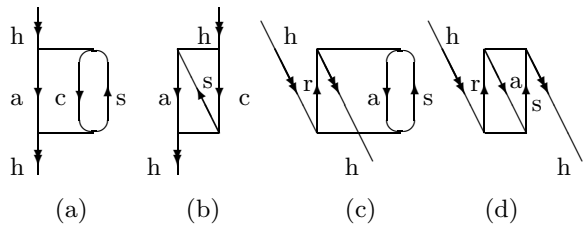

FIG. 1. Illustration of the second order energy contributions to a one-hole system. Diagrams (a) and (b) show fluctuations to two holes and one excited orbital and diagrams (c) and (d) double excitations (correlation). Down-pointing single arrows denote core orbitals, down-pointing double arrows denote the hole, and up-pointing arrows denote excited orbitals.

ing and the excitation from an orbital preserves its angular symmetry. The lowest order relaxation correction to an orbital b can consequently be written

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

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

$$\sum_b^{\mathrm{core}} \langle\{bh\}\mid V_{12}\mid\{\rho_b^{\mathrm{relax}}h\}\rangle. \quad (2)$$

In this way, all types of diagrams in Figs. 1(a) and 1(b) with either orbital $a=h$ (and $b=c$) or $c=h$ (and $b=a$) and $\ell_s=\ell_b$ and $j_s=j_b$ are included, i.e., the single excitations that preserve the angular structure. It can be noted that these 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 nonrelativistic 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 the diagram in 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 $c\to\infty$. The problem comes instead from the spin-angular part. Since

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

decoupling of spin and orbital angular momenta cannot be done without summing over all total angular momenta, j. An unambiguous way to see how this influences our example in Fig. 1(a) with orbital $a=h$ and $\ell_s=\ell_b$ is to compare the angular contribution nonrelativistically 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 wave functions. Nonrelativistically, the angular part can be evaluated as

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

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

$$\sum_b^{\mathrm{core}}\sum_k\sum_{j_{h'}}^{\ell_h\pm1/2}\sum_{j_{b'}}^{\ell_b\pm1/2}\frac{1}{2k+1}\frac{1}{2j_h+1}\langle j_h\|\mathbf{C}^k\|j_{h'}\rangle^2 \times\langle j_b\|\mathbf{C}^k\|j_{b'}\rangle^2. \quad (6)$$

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

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

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, Eq. (2), to the relaxation gives an unphysical fine-structure offset of 0.024 eV in the $c\to\infty$ 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 [4,5] the corrected value reaches ~ -0.050 eV, in line with the MCDF Coulomb relaxation contribution of ~ -0.049 eV, listed in the third section of 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 nonrelativistic 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 nonrelativistic result in a relativistic framework. In RMBPT the full contribution from Figs. 1(a) and 1(b) produces no N.R. offset, but any attempt to speed up the

TABLE I. Summary of the contributions to Be-like Ar FSS. 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].

	$2p_{1/2}$	$2p_{3/2}$	Δ
Contributions			
Ne-like DF orbital energy	426.500 02	424.132 11	2.367 91
Δ DF Breit	−0.226 59	−0.135 76	−0.090 83
Higher order retardation	−0.000 11	0.000 79	−0.000 90
QED correlation	0.013 53	0.007 55	0.005 98
Contributions specific to RMBPT			
Second order core-core, Coulomb	−4.485 09	−4.425 87	−0.059 21
core-core, Breit	−0.011 87	−0.008 14	−0.003 73
Correlation, Coulomb	2.567 26	2.557 63	0.009 62
Correlation, Breit	0.023 91	0.020 18	0.003 73
Higher order contribution (Coul. + Breit)	0.165 59	0.158 85	0.006 74
Δ DF-Breit orbitals	0.001 98	0.000 43	0.001 56
Total (RMBPT)	424.548 63	422.307 77	2.240 86
Experiment			2.240 10
Contributions specific to MCDF (N.R. offset subtracted)			
Relaxation (Coulomb)	−3.108 00	−3.059 31	−0.048 69
Relaxation (Breit)	−0.004 06	−0.003 14	−0.000 92
Correlation (Coul. $\rightarrow 5g$)	1.424 66	1.396 04	0.028 62
Correlation (Breit $\rightarrow 5g$)	−0.013 59	0.007 41	−0.021 00
Total (MCDF)	424.585 85	422.345 69	2.240 16
Experiment			2.240 10

convergence of the perturbation expansion by singling out the important subclass that involve only single-particle energy denominators as in Eq. (1) will do so. The RMBPT results shown in Table I are obtained without any such procedure and have a correct nonrelativistic limit by construction.

With several configurations included it should, in principle, be possible to reach the correct nonrelativistic 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 to truncate after double excitations from the dominating configuration, but just as double excitations are needed to be added to the single excitations to obtain the correct nonrelativistic limit, triple excitations will be needed to be added to corresponding double excitations and so on. Since higher multiple excitations are less important, the remaining offset will, however, decrease steadily.

We now proceed to demonstrate the vanishing of the nonrelativistic offset in an essentially complete MCDF calculation. In the present calculation we have added to the original configuration all single and double excitations up to a given maximum n and ℓ. Note that one has to be careful in considering the meaning of single and double excitations. 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 five 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 $2p_{1/2}^2 2p_{3/2}^2 3p_{3/2}$). We went from $3d$ to $5g$ for the case with a normal speed of light, and up to $6h$ for the nonrelativistic limit. This represents, respectively, 299, 1569, 4339, and 9127 fully relaxed jj configurations for the $J = 1/2$ case, and 456, 2541, 7356, and 15 915 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 ''Brillouin single excitations,'' i.e., those that should contribute only in third order, as stated by Brillouin's theorem [9–11]. These excitations are often excluded since they complicate the numerical convergence. Again we use here Brillouin's theorem in the jj sense; i.e., we exclude all configurations transformed from the initial one by replacing an orbital with quantum numbers n, κ by one with n', κ, where κ 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 between electrons used in the evaluation of wave functions and energies, and once with the full Breit interaction in the evaluation of wave functions and mixing coefficients. This allows one 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 in 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 nonzero con-

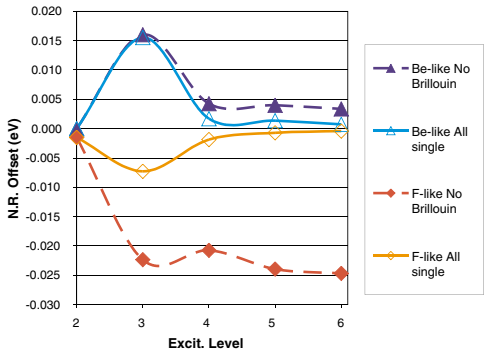

FIG. 2 (color online). A comparison of the nonrelativistic offset for Be-like and F-like argon, evaluated including all single excitations, or only those not obeying Brillouin's theorem.

stant 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 nonrelativistic offset with and without Brillouin configurations are presented in Table II. When comparing both results, it is clear that excluding Brillouin single excitations and then subtracting the N.R. offset leads to the same result as including the Brillouin configurations. The agreement with experiment and with RMBPT results is excellent in both cases, even though the quality of the convergence when including all single excitations is not as good as when Brillouin ones are excluded. Moreover, the inclusion of all single excitations also enables one to correct the energy of a level as shown in Table III, which was not possible with the subtraction method. Finally, we note 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.

TABLE II. Contributions to the MCDF FSS energy affected by the N.R. offset (eV). "ΔE doub. Exc. $\rightarrow n = i$": correlation energy for the configuration space which includes all double excitations up to principal quantum number $n = i$. Rel. val.: relativistic value; N.R. Off.: offset obtained at the nonrelativistic limit.

	Rel. val.	N.R. off.	Difference
Dirac-Fock Coulomb	2.316 26	−0.001 48	2.317 74
Brillouin single excitations excluded			
ΔE Exc. $\rightarrow n = 3$	−0.018 55	−0.020 86	0.002 31
ΔE Exc. $\rightarrow n = 4$	−0.014 21	−0.019 26	0.005 05
ΔE Exc. $\rightarrow n = 5$	−0.016 41	−0.022 47	0.006 06
Total	2.216 21	−0.023 95	2.240 16
Difference with exp	−0.023 89		0.000 06
All single and double excitations included			
ΔE Exc. $\rightarrow n = 3$	−0.003 71	−0.005 82	0.002 11
ΔE Exc. $\rightarrow n = 4$	0.004 45	−0.000 37	0.004 82
ΔE Exc. $\rightarrow n = 5$	0.006 61	0.000 75	0.005 86
Total (SES Welton)	2.239 23	−0.000 73	2.239 96
Difference with exp	−0.000 87		−0.000 14

TABLE III. Change in the ground state ($J = 3/2$) correlation energy due to Brillouin single excitation.

Configuration	No Brillouin	All single	Difference
corr. $\rightarrow 3d$	−5.1792	−5.1989	−0.0196
corr. $\rightarrow 4f$	−7.7349	−7.7603	−0.0255
corr. $\rightarrow 5g$	−8.6551	−8.6871	−0.0320

In conclusion, we have proven, by comparing RMBPT and MCDF results, that the N.R. offset is due to relaxation 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 *all single* configurations are included. In practice, excluding Brillouin single excitations and then subtracting the N.R. offset leads to the same value, but numerical convergence of the self-consistent field process is much easier in the latter case. Finally, failing to account for the N.R. offset leads to poor results, even at a moderately large Z, a fact that may not have received enough attention in many MCDF calculations. The present work also shows that similar problems can happen in RMBPT calculations if subclasses of important effects are singled out and by themselves are treated to higher order. The improved convergence will then come at the expense of an N.R. offset. This fact had not been recognized before.

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