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2011 J. Phys. B: At. Mol. Opt. Phys. 44 175003

(http://iopscience.iop.org/0953-4075/44/17/175003)

J. Phys. B: At. Mol. Opt. Phys. **44** (2011) 175003 (11pp) doi:10.1088/0953-4075/44/17/175003

Tensorial form and matrix elements of the relativistic nuclear recoil operator

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Received 10 June 2011, in final form 8 July 2011
Published 18 August 2011
Online at stacks.iop.org/JPhysB/44/175003

Abstract
Within the lowest-order relativistic approximation ($\sim v^2/c^2$) and to first order in m_e/M, the tensorial form of the relativistic corrections of the nuclear recoil Hamiltonian is derived, opening interesting perspectives for calculating isotope shifts in the multiconfiguration Dirac–Hartree–Fock framework. Their calculation is illustrated for selected Li-, B- and C-like ions. This work underlines the fact that the relativistic corrections to the nuclear recoil are definitively necessary for obtaining reliable isotope shift values.

1. Introduction

Nuclear and relativistic effects in atomic spectra are treated in the pioneering works of Stone [1, 2] and Veseth [3]. The theory of the mass shift has then been reformulated by Palmer [4]. Calculations of nuclear motional effects in many-electron atoms have been performed by Parpia and co-workers [5, 6] in the relativistic scheme, using fully relativistic wavefunctions, but adopting the non-relativistic form of the recoil operator. Relativistic nuclear recoil corrections to the energy levels of multicharged ions have been estimated by Shabaev and Artemyev [7] who derived the relativistic corrections of the recoil Hamiltonian. In a study of isotope shifts of forbidden transitions in Be- and B-like argon ions, Tupitsyn *et al* [8] showed that a proper evaluation of the mass isotope shift requires the use of this relativistic recoil operator. The latter has also been shown to be crucial by Porsev *et al* [9] for calculating isotope shifts of transitions between the fine structure energy levels of the ground multiplets of Fe I and Fe II.

As far as computational atomic structure is concerned, the extension of the available relativistic codes such as GRASP2K [10] or MCDF-gme [11, 12] is needed for estimating these mass corrections properly for any many-electron system. Programs to calculate pure angular momentum coefficients for any scalar one- and two-particle operator are available [13] but do require the knowledge of the tensorial structure of the operators to be integrated between the many-electron atomic wavefunctions [14]. The tensorial form of the nuclear recoil Hamiltonian is derived in this work, opening interesting perspectives for calculating isotope shifts in the multiconfiguration Dirac–Hartree–Fock (MCDHF) framework.

2. The relativistic mass shift operator

In the MCDHF method, the atomic state function (ASF) $\Psi(\gamma P J M_J)$, of a stationary state of an atom, is expressed as a linear combination of symmetry-adapted configuration state functions (CSFs) $\Phi(\gamma_p P J M_J)$, i.e.

$$\Psi(\gamma P J M_J) = \sum_p c_p \Phi(\gamma_p P J M_J), \qquad (1)$$

where J is the total electronic angular momentum of the state, γ represents the electronic configuration and intermediate quantum numbers, and P stands for the parity. The mixing coefficients c_p and the one-electron radial wavefunctions spanning the CSFs are optimized by solving the MCDHF equations iteratively until self-consistency. The latter are

derived by applying the variational principle to the energy functional based on the Dirac–Coulomb Hamiltonian [14]

$$H_{\rm DC} = \sum_{i=1}^{N} \left(c\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta_i - 1)c^2 + V(r_i) \right) + \sum_{i<j}^{N} \frac{1}{r_{ij}}, \quad (2)$$

where $V(r_i)$ is the monopole part of the electron–nucleus interaction, $\boldsymbol{\alpha}$ and β are the (4×4) Dirac matrices and c is the speed of light ($c = 1/\alpha$ in atomic units, where α is the fine-structure constant).

The mass shift of the energy levels in an atom with nuclear mass M is caused by the recoil motion of the atomic nucleus. The corresponding recoil Hamiltonian

$$H_{\rm MS} = \frac{1}{2M} \sum_{i,j}^{N} \left(\boldsymbol{p}_i \cdot \boldsymbol{p}_j - \frac{\alpha Z}{r_i} \left(\boldsymbol{\alpha}_i + \frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{r}_i)\, \boldsymbol{r}_i}{r_i^2} \right) \cdot \boldsymbol{p}_j \right) \quad (3)$$

has been derived within the lowest-order relativistic approximation and to first order in m/M by Shabaev and collaborators [7, 8]. Rewriting it as the sum of the normal mass shift (NMS) and specific mass shift (SMS) contributions and using the tensorial form $\boldsymbol{r}^1 = r\boldsymbol{C}^1$, (3) becomes

$$H_{\rm MS} = H_{\rm NMS} + H_{\rm SMS}, \quad (4)$$

with

$$H_{\rm NMS} = \frac{1}{2M} \sum_{i=1}^{N} \left(\boldsymbol{p}_i^2 - \frac{\alpha Z}{r_i} \boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i - \frac{\alpha Z}{r_i} \left(\boldsymbol{\alpha}_i \cdot \boldsymbol{C}_i^1 \right) \boldsymbol{C}_i^1 \cdot \boldsymbol{p}_i \right), \quad (5)$$

$$H_{\rm SMS} = \frac{1}{M} \sum_{i<j}^{N} \left(\boldsymbol{p}_i \cdot \boldsymbol{p}_j - \frac{\alpha Z}{r_i} \boldsymbol{\alpha}_i \cdot \boldsymbol{p}_j - \frac{\alpha Z}{r_i} \left(\boldsymbol{\alpha}_i \cdot \boldsymbol{C}_i^1 \right) \boldsymbol{C}_i^1 \cdot \boldsymbol{p}_j \right), \quad (6)$$

that, in both cases, are rewritten as a sum of three separate contributions:

$$H_{\rm NMS} \equiv H_{\rm NMS}^1 + H_{\rm NMS}^2 + H_{\rm NMS}^3 \quad (7)$$

and

$$H_{\rm SMS} \equiv H_{\rm SMS}^1 + H_{\rm SMS}^2 + H_{\rm SMS}^3. \quad (8)$$

Since the expectation values of the NMS and SMS operators are evaluated with the MCDHF wavefunctions, the expectation values $\langle H_{\rm NMS}^1 \rangle$ and $\langle H_{\rm SMS}^1 \rangle$ partly contain the relativistic contributions. Tupitsyn *et al* [8] pointed out that averaging the non-relativistic recoil operator with the relativistic wavefunctions strongly overestimates the relativistic correction to the recoil effect such that it becomes important to use the complete form (3) when one works in the relativistic scheme.

2.1. NMS expectation value

The (mass-independent) NMS parameter $K_{\rm NMS}$ is defined by the following expression:

$$\frac{K_{\rm NMS}}{M} \equiv \langle \Psi(\gamma P J M_J) | H_{\rm NMS} | \Psi(\gamma P J M_J) \rangle. \quad (9)$$

By analogy with (7), we define $K_{\rm NMS}$ as the sum of $K_{\rm NMS} = K_{\rm NMS}^1 + K_{\rm NMS}^2 + K_{\rm NMS}^3$. Applying the Wigner–Eckart theorem [15], the matrix element of the NMS operator is M_J-invariant and is proportional to the reduced matrix element (r.m.e.)[5]

$$\frac{K_{\rm NMS}}{M} = \frac{1}{\sqrt{2J+1}} \langle \Psi(\gamma P J) \| H_{\rm NMS} \| \Psi(\gamma P J) \rangle = [\Psi(\gamma P J) \| H_{\rm NMS} \| \Psi(\gamma P J)]\,. \quad (10)$$

Using multiconfiguration expansions (1), the reduced matrix elements of the general spherical tensor operator T_q^k becomes

$$[\Psi(\gamma P J) \| \boldsymbol{T}^k \| \Psi(\gamma P J)] = \sum_{p,s} c_p c_s [\Phi(\gamma_p P J) \| \boldsymbol{T}^k \| \Phi(\gamma_s P J)]. \quad (11)$$

The reduced matrix elements of the one-electron operator $\boldsymbol{T}^k = \sum_i \boldsymbol{t}^k(i)$ between CSFs are expressed as a sum over single-particle reduced matrix elements

$$[\Phi(\gamma_p P J) \| \boldsymbol{T}^k \| \Phi(\gamma_s P J)] = \sum_{a,b} T_{ps}(ab) [n_a \kappa_a \| \boldsymbol{t}^k \| n_b \kappa_b], \quad (12)$$

where the $T_{ps}(ab)$ are the spin-angular coefficients arising from Racah's algebra [13, 14, 16]. Introducing the one-body NMS operator associated with (5) ($H_{\rm NMS} = \sum_i h_{\rm NMS}(i)$)

$$h_{\rm NMS} = \frac{1}{2M} \left(\boldsymbol{p}^2 - \frac{\alpha Z}{r} \left(\boldsymbol{\alpha} + \left(\boldsymbol{\alpha} \cdot \boldsymbol{C}^1 \right) \boldsymbol{C}^1 \right) \cdot \boldsymbol{p} \right), \quad (13)$$

we hereafter derive the expression of its r.m.e., using relativistic central-field one-electron wavefunctions

$$\psi_{n_a,\kappa_a,m_a}(\boldsymbol{r}, \sigma) = \frac{1}{r} \begin{pmatrix} P_{n_a,\kappa_a}(r) \Omega_{\kappa_a,m_a}(\theta, \phi, \sigma) \\ i\, Q_{n_a,\kappa_a}(r) \Omega_{-\kappa_a,m_a}(\theta, \phi, \sigma) \end{pmatrix}. \quad (14)$$

P_a and Q_a are respectively the large and small components of the relativistic one-electron radial wavefunction $a = (n_a \kappa_a)$, where $\kappa = (l - j)(2j + 1)$.

Introducing the notation $\partial_r \equiv \frac{\partial}{\partial r}$, the action of the operator $\boldsymbol{p}^2$ on the large ($F = P$) and the small ($F = Q$) component of a relativistic wavefunction

$$\boldsymbol{p}^2 \frac{F_{n,\kappa}(r)}{r} \Omega_{\kappa,m}(\theta, \phi, \sigma) = \frac{1}{r} \left(-\partial_r^2 + \frac{l(l+1)}{r^2} \right) F_{n,\kappa}(r) \Omega_{\kappa,m}(\theta, \phi, \sigma) \quad (15)$$

is found using

$$\boldsymbol{p}^2 = -\Delta = -\frac{1}{r^2} \partial_r r^2 \partial_r + \frac{\boldsymbol{l}^2}{r^2}. \quad (16)$$

[5] The two definitions of r.m.e. are related to each other through $\langle \gamma J' \| O^k \| \gamma J \rangle = \sqrt{2J'+1}\, [\gamma J' \| O \| \gamma J]$.

From this expression and integrating by parts, the first term of the one-electron matrix element NMS operator (13) becomes

$$\langle n_a\kappa_a m_a|\frac{\boldsymbol{p}^2}{2}|n_b\kappa_b m_b\rangle = \delta(\kappa_a m_a, \kappa_b m_b) \times \frac{1}{2}\int_0^\infty \mathrm{d}r\left((\partial_r P_a)(\partial_r P_b) + (\partial_r Q_a)(\partial_r Q_b) + \frac{l_b(l_b+1)P_aP_b + \widetilde{l}_b(\widetilde{l}_b+1)Q_aQ_b}{r^2}\right), \quad (17)$$

with $\widetilde{l} = 2j - l$. Building the Dirac matrices $\boldsymbol{\alpha}$ from $\boldsymbol{\alpha} = \sigma_x \otimes \boldsymbol{\sigma}$ with

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad (18)$$

one rewrites the second and the third parts of the NMS operator (13) as

$$\left(\frac{-\alpha Z}{2r}\right)(\boldsymbol{\alpha}\cdot\boldsymbol{p} + (\boldsymbol{\alpha}\cdot\boldsymbol{C}^1)(\boldsymbol{C}^1\cdot\boldsymbol{p})) \equiv \sigma_x \otimes A = \begin{pmatrix} 0 & A \\ A & 0 \end{pmatrix} \quad (19)$$

with

$$A = \left(\frac{-\alpha Z}{2r}\right)\left(\boldsymbol{\sigma}\cdot\boldsymbol{p} + (\boldsymbol{\sigma}\cdot\boldsymbol{C}^1)(\boldsymbol{C}^1\cdot\boldsymbol{p})\right). \quad (20)$$

Taking into account that (see (A.4.9) and (3.2.14) in [14])

$$\boldsymbol{\sigma}\cdot\boldsymbol{C}^1 = \boldsymbol{\sigma}\cdot\boldsymbol{e}_r = \sigma_r; \qquad \boldsymbol{C}^1\cdot\boldsymbol{p} = \boldsymbol{e}_r\cdot\boldsymbol{p} = (-i\partial_r), \quad (21)$$

and

$$\boldsymbol{\sigma}\cdot\boldsymbol{p} = -i\sigma_r\left(\partial_r + \frac{K+1}{r}\right), \quad (22)$$

with $K = -(1 + \boldsymbol{\sigma}\cdot\boldsymbol{l})$, the operator A becomes

$$A = \left(\frac{-\alpha Z}{2r}\right)(-i\sigma_r)\left(2\partial_r + \frac{K+1}{r}\right). \quad (23)$$

Acting on the one-electron relativistic wavefunction component, it gives

$$A\frac{F_{n,\kappa}(r)}{r}\Omega_{\kappa,m} = \left(\frac{-\alpha Z}{2r}\right)\frac{i}{r}\left(2\partial_r + \frac{\kappa-1}{r}\right)F_{n,\kappa}(r)\Omega_{-\kappa,m}, \quad (24)$$

from which one derives, integrating by parts, the one-electron matrix element of the second and third parts of the NMS operator

$$\langle n_a\kappa_a m_a|\sigma_x\otimes A|n_b\kappa_b m_b\rangle = \delta(\kappa_a m_a, \kappa_b m_b) \times \frac{1}{2}\int_0^\infty \left((-2\alpha Z)\frac{Q_a\partial_r P_b + Q_b\partial_r P_a}{r} + (-\alpha Z)\left(\frac{\kappa_b - 1}{r^2}\right)(P_bQ_a + P_aQ_b)\right)\mathrm{d}r. \quad (25)$$

Combining (17) and (25) to deduce the r.m.e. of the NMS operator (13), we obtain the final expression

$$[n_a\kappa_a\|h_{\mathrm{NMS}}\|n_b\kappa_b] = \delta(\kappa_a,\kappa_b) \times \frac{1}{2M}\int_0^\infty \left((\partial_r P_a)(\partial_r P_b) + (\partial_r Q_a)(\partial_r Q_b) + \frac{l_b(l_b+1)P_aP_b + \widetilde{l}_b(\widetilde{l}_b+1)Q_aQ_b}{r^2} + (-2\alpha Z)\frac{Q_a\partial_r P_b + Q_b\partial_r P_a}{r} + (-\alpha Z)\left(\frac{\kappa_b-1}{r^2}\right)(Q_aP_b + Q_bP_a)\right)\mathrm{d}r. \quad (26)$$

2.2. SMS expectation value

Similarly to (10), the (mass-independent) SMS parameter K_{SMS} is defined as

$$\frac{K_{\mathrm{SMS}}}{M} \equiv [\Psi(\gamma PJ)\|H_{\mathrm{SMS}}\|\Psi(\gamma PJ)], \quad (27)$$

and K^1_{SMS}, K^2_{SMS}, K^3_{SMS} as its contributions according to (8). Its evaluation requires the calculation of the corresponding matrix elements in the CSF space. For the general scalar two-particle operator

$$G = \sum_{i<j} g(i,j) \quad (28)$$

with

$$g(i,j) = \sum_k g_k(r_i,r_j)\left(\mathbf{T}^k(i)\cdot\mathbf{T}^k(j)\right), \quad (29)$$

the reduction of the many-electron r.m.e. in terms of the two-electron integrals X^k, also called *effective interaction strengths* [14],

$$[\Phi(\gamma_p PJ)\|\sum_{i<j} g(i,j)\|\Phi(\gamma_s PJ)] = \sum_{abcd}\sum_k v^{(k)}_{ps}(abcd)X^k(abcd) \quad (30)$$

can be performed using Racah's algebra [13, 14, 16]. For the SMS Hamiltonian (6), using $k = 1$, all three terms have the particular form

$$g(i,j) = g_1(r_i)g_1(r_j)\left(\mathbf{T}^1(i)\cdot\mathbf{T}^1(j)\right) \quad (31)$$

in which the radial part $g_1(r_i,r_j)$ of (29) is factorized. Adopting the covariant notation for the $3j$-symbol of Wigner [17] and using the definition of the scalar product of two irreducible tensor operators and the Wigner–Eckart theorem, the matrix element of (31) can be written as follows:

$$\langle ab|g(i,j)|cd\rangle = \sum_{q=-1}^{1}\begin{pmatrix} m_a & 1 & j_c \\ j_a & q & m_c\end{pmatrix} \times \begin{pmatrix} m_b & q & j_d \\ j_b & 1 & m_d\end{pmatrix} X^1(abcd), \quad (32)$$

where

$$X^1(abcd) = -\langle a\|g(r_i)\boldsymbol{T}^1(i)\|c\rangle\langle b\|g(r_j)\boldsymbol{T}^1(j)\|d\rangle. \quad (33)$$

From the structure of (8), the latter has three components

$$X^1(abcd) = X^1_1(abcd) + X^1_2(abcd) + X^1_3(abcd) \quad (34)$$

that we analysed hereafter separately.

2.2.1. First part: $X_1^1(abcd)$. Building $X_1^1(abcd)$ from (33), we have

$$g(r_i)\boldsymbol{T}^1(i) = \boldsymbol{p}^1(i); \qquad g(r_j)\boldsymbol{T}^1(j) = \boldsymbol{p}^1(j). \tag{35}$$

Introducing the one-electron reduced matrix element

$$\langle a\|\boldsymbol{p}^1\|c\rangle = -i\langle\kappa_a\|\boldsymbol{C}^1\|\kappa_c\rangle\mathcal{V}(n_a\kappa_a, n_c\kappa_c), \tag{36}$$

where $\mathcal{V}(n\kappa, n'\kappa')$ is the Vinti radial integral

$$\begin{aligned}\mathcal{V}(n\kappa, n'\kappa') &= \int_0^\infty P_{n\kappa}(r)\left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{\kappa(\kappa+1)-\kappa'(\kappa'+1)}{2r}\right]P_{n'\kappa'}(r)\,\mathrm{d}r \\ &+ \int_0^\infty Q_{n\kappa}(r)\left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{-\kappa(-\kappa+1)+\kappa'(-\kappa'+1)}{2r}\right] \\ &\times Q_{n'\kappa'}(r)\,\mathrm{d}r,\end{aligned} \tag{37}$$

the first contribution to the effective interaction strength is written as

$$\begin{aligned}X_1^1(abcd) &= \langle\kappa_a\|\boldsymbol{C}^1\|\kappa_c\rangle\langle\kappa_b\|\boldsymbol{C}^1\|\kappa_d\rangle \\ &\times \mathcal{V}(n_a\kappa_a, n_c\kappa_c)\mathcal{V}(n_b\kappa_b, n_d\kappa_d),\end{aligned} \tag{38}$$

recovering the uncorrected relativistic expression used in [5, 6].

2.2.2. Second part: $X_2^1(abcd)$. For the second term of the SMS operator, we identify from (6), (8), (33) and (34)

$$g(r_i)\boldsymbol{T}^1(i) = \frac{-\alpha Z}{r}\left(\sigma_x \otimes \boldsymbol{\sigma}^1(i)\right); \quad g(r_j)\boldsymbol{T}^1(j) = \boldsymbol{p}^1(j). \tag{39}$$

Introducing the matrix element

$$\begin{aligned}\langle a|r^{-1}\left(\sigma_x \otimes \boldsymbol{\sigma}_q^1\right)|c\rangle &= i\int_0^\infty \frac{\mathrm{d}r}{r}\big(-Q_a P_c\langle-\kappa_a m_a|\boldsymbol{\sigma}_q^1|\kappa_c m_c\rangle \\ &+ Q_c P_a\langle\kappa_a m_a|\boldsymbol{\sigma}_q^1|-\kappa_c m_c\rangle\big),\end{aligned} \tag{40}$$

and using the r.m.e. (36), the corresponding contribution to the effective interaction strength is

$$\begin{aligned}X_2^1(abcd) &= -\langle\kappa_b\|\boldsymbol{C}^1\|\kappa_d\rangle\mathcal{V}(n_b\kappa_b, n_d\kappa_d) \\ &\times \int_0^\infty \mathrm{d}r\left(\frac{-\alpha Z}{r}\right)\big(-Q_a P_c\langle-\kappa_a\|\boldsymbol{\sigma}^1\|\kappa_c\rangle \\ &+ Q_c P_a\langle\kappa_a\|\boldsymbol{\sigma}^1\|-\kappa_c\rangle\big).\end{aligned} \tag{41}$$

2.2.3. Third part: $X_3^1(abcd)$. Similarly, the two components of the third term of the SMS operator are

$$\begin{aligned}&g(r_i)\boldsymbol{T}^1(i) = \frac{-\alpha Z}{r}\left(\sigma_x \otimes (\sigma_r(i)\boldsymbol{C}^1(i))\right); \\ &g(r_j)\boldsymbol{T}^1(j) = \boldsymbol{p}^1(j).\end{aligned} \tag{42}$$

Using the matrix element

$$\begin{aligned}&\langle a|r^{-1}\left(\sigma_x \otimes \left(\sigma_r\boldsymbol{C}_q^1\right)\right)|c\rangle \\ &= i\int_0^\infty \frac{\mathrm{d}r}{r}\big(Q_a P_c\langle-\kappa_a m_a|\boldsymbol{C}_q^1|-\kappa_c m_c\rangle \\ &- Q_c P_a\langle\kappa_a m_a|\boldsymbol{C}_q^1|\kappa_c m_c\rangle\big),\end{aligned} \tag{43}$$

and the r.m.e. (36), the third contribution to the effective interaction strength takes the form

$$\begin{aligned}X_3^1(abcd) &= -\langle\kappa_b\|\boldsymbol{C}^1\|\kappa_d\rangle\langle\kappa_a\|\boldsymbol{C}^1\|\kappa_c\rangle\mathcal{V}(n_b\kappa_b, n_d\kappa_d) \\ &\times \int_0^\infty \mathrm{d}r\left(\frac{-\alpha Z}{r}\right)(Q_a P_c - Q_c P_a),\end{aligned} \tag{44}$$

where we take advantage of $\langle-\kappa_a\|\boldsymbol{C}^k\|-\kappa_c\rangle = \langle\kappa_a\|\boldsymbol{C}^k\|\kappa_c\rangle$.

2.3. Useful one-electron reduced matrix elements

Equations (26), (38), (41) and (44) are the final key expressions of the relativistic mass shift one-electron r.m.e. that involve the following three reduced angular one-electron matrix elements

$$\begin{aligned}\langle\kappa_a\|\boldsymbol{C}^1\|\kappa_c\rangle &= (-1)^{j_a+1/2}\sqrt{[j_a, j_c]}\begin{pmatrix} j_a & 1 & j_c \\ 1/2 & 0 & -1/2\end{pmatrix} \\ &\times \pi(l_a, l_c, 1),\end{aligned} \tag{45}$$

$$\begin{aligned}\langle-\kappa_a\|\boldsymbol{\sigma}^1\|\kappa_c\rangle &= \delta(\widetilde{l}_a, l_c)(-1)^{\widetilde{l}_a+1/2+j_a+1}\sqrt{6[j_a, j_c]} \\ &\times \begin{Bmatrix} 1/2 & j_a & \widetilde{l}_a \\ j_c & 1/2 & 1\end{Bmatrix},\end{aligned} \tag{46}$$

$$\begin{aligned}\langle\kappa_a\|\boldsymbol{\sigma}^1\|-\kappa_c\rangle &= \delta(l_a, \widetilde{l}_c)(-1)^{l_a+1/2+j_a+1}\sqrt{6[j_a, j_c]} \\ &\times \begin{Bmatrix} 1/2 & j_a & l_a \\ j_c & 1/2 & 1\end{Bmatrix},\end{aligned} \tag{47}$$

where $\pi\ (l_a, l_c, 1)$ is defined by

$$\pi\ (l_a, l_c, 1) = \begin{cases} 1 & \text{if } l_a + 1 + l_c \text{ even}, \\ 0 & \text{otherwise.}\end{cases} \tag{48}$$

3. Applications

We wrote a new program, hereafter referred to as RMS2, for estimating the expectation values of the relativistic nuclear recoil operators using MCDHF wavefunctions calculated with the GRASP2K package [10]. This code is based on the previous program SMS92 [6] in which

- for the NMS, the one-electron radial integrals (expression (39) of the original paper [6]) are replaced by the corresponding relativistic expression (26),
- for the SMS, the first contribution $X_1^1(abcd)$ (expression (40) of the original paper [6]) is corrected by adding the relativistic contributions (41) and (44).

It is important to note that the program SMS92 calculates the uncorrected NMS as the expectation value $\langle\sum_i T_i\rangle$, where T_i is the Dirac kinetic energy operator $T_i = c\boldsymbol{\alpha}_i\cdot\boldsymbol{p}_i + (\beta_i - 1)c^2$ associated with electron i, while the program RMS2 uses more accurately $\langle H_{\mathrm{NMS}}^1\rangle = \langle\sum_i p_i^2/2M\rangle$, which is consistent with section 2.1. An equivalent version has been written for the code MCDF-gme.

In this work, we evaluate the NMS and SMS parameters (9) and (27) for some low-lying levels of neutral lithium, boron-like argon and two medium-Z carbon-like ions (Ca XV and Sc XVI) to investigate the importance of the relativistic corrections. The nuclear charge distribution is described by a Fermi model. Nuclear masses (M_N) are calculated by taking away the mass of the electrons and the binding energy from the atomic mass (M_A), using the formula

$$M_N(A, Z) = M_A(A, Z) - Zm_e + B_{el}(Z) \tag{49}$$

where the total binding energy of the electrons (expressed in eV) is estimated using [18, 19]

$$B_{el}(Z) = 14.4381Z^{2.39} + 1.554\,68\times10^{-6}Z^{5.35}. \tag{50}$$

Table 1. Atomic masses (M_A) [20] and nuclear masses (M_N) (in u) calculated from (49) and (50) for lithium and argon isotopes.

Isotope	M_A	M_N
^{6}Li	6.015 122 795(16)	6.013 867 37
^{7}Li	7.016 004 55(8)	7.014 749 07
^{36}Ar	35.967 545 106(29)	35.957 6862
^{40}Ar	39.962 383 1225(29)	39.952 5242

The atomic and nuclear masses relevant to this work are reported in table 1.

When discussing a transition mass isotope shift, one needs to consider the variation of the mass parameter from one level to another. The line k frequency isotope shift, $\delta\nu_k^{A_1,A_2} = \left(\delta E_j^{A_1,A_2} - \delta E_i^{A_1,A_2}\right)/h$, between the isotopes A_1 and A_2, of nuclear masses M_1 and M_2, respectively, is usually written as the sum of the NMS, SMS and field shift (FS) contributions:

$$\delta\nu_k^{A_1,A_2} = \underbrace{\delta\nu_{k,\mathrm{NMS}}^{A_1,A_2} + \delta\nu_{k,\mathrm{SMS}}^{A_1,A_2}}_{\delta\nu_{k,\mathrm{MS}}^{A_1,A_2}} + \delta\nu_{k,\mathrm{FS}}^{A_1,A_2}, \tag{51}$$

with

$$\delta\nu_{k,\mathrm{MS}}^{A_1,A_2} = \left(\frac{M_2 - M_1}{M_1 M_2}\right)\frac{\Delta K_{\mathrm{MS}}}{h} = \left(\frac{M_2 - M_1}{M_1 M_2}\right)\Delta\widetilde{K}_{\mathrm{MS}}, \tag{52}$$

where ΔK_{MS} is the difference of the K_{MS} parameters of the levels involved in transition k. As far as conversion factors are concerned, we use[6] $\Delta\widetilde{K}_{\mathrm{MS}}[\mathrm{GHz\,u}] = 3609.4824\Delta K_{\mathrm{MS}}[m_e E_\mathrm{h}]$. Note that thanks to the separability enhanced in (4), (52) can be applied to both the mass contributions NMS and SMS, separately.

3.1. Hydrogen-like selenium

Below we present some relevant calculations of expression (26) for a heavy one-electron ion (Se XXXIV, $Z = 34$). This choice is motivated by the interesting comparison with the unpublished work of Kozlov [22]. The NMS values calculated with the operators H^1_{NMS} and $\left(H^2_{\mathrm{NMS}} + H^3_{\mathrm{NMS}}\right)$, using the RMS2 program, are reported in table 2. In the second and third column, respectively, comparison is made with the numerical results of Kozlov together with our analytical values. The latter are based on analytical hydrogenic wavefunctions[7] [23] and are in complete agreement with the values of the analytical formulas derived for hydrogenic systems in [7]. Note that these formulas show that the relativistic corrections arising from the non-relativistic and relativistic recoil operators contain similar terms which, being rapidly growing when Z increases, cancel each other as discussed in [24] for Li-like ions.

[6] This conversion factor is calculated as $(m_e/\mathrm{u})2R_\infty c \times 1.10^{-9} = 3609.4824$ using the 2006 CODATA recommended values of the fundamental physical constants [21].

[7] The values reported in tables 2 and 3 are based on $\alpha^{-1} = 137.035\,989\,500$ adopted in GRASP2K. For $1s_{1/2}$, the analytical result for K_{NMS} becomes 656.358 886 872 if adopting the $\alpha^{-1} = 137.035\,999\,679\,2006$ CODATA value [21].

Table 2. Contributions to the NMS K_{NMS} parameters (in $m_e E_\mathrm{h}$) for hydrogen-like selenium ($Z = 34$).

	RMS2	Kozlov [22]	Analytic
		K^1_{NMS}	
$1s_{1/2}$	656.358 9797	656.3589	656.358 899 684
$2p_{1/2}$	154.893 7900	154.8938	154.893 789 883
$2p_{3/2}$	147.519 2507	147.5192	147.519 250 700
		$K^2_{\mathrm{NMS}} + K^3_{\mathrm{NMS}}$	
$1s_{1/2}$	−78.358 8949	−78.3589	−78.358 899 6839
$2p_{1/2}$	−8.098 7869	−8.0988	−8.098 786 8710
$2p_{3/2}$	−3.019 2507	−3.0193	−3.019 250 6997

3.2. Lithium-like systems using Dirac one-electron wavefunctions

The SMS parameters for Li-like iron ($Z = 26$) and selenium ($Z = 34$) are calculated in the single configuration approximation using three-electron wavefunctions built on unscreened Dirac solutions. The results are reported in table 3 and compared with independent estimations using an adapted version of MCDF-gme [11, 25] and with the analytical results. The three sets are consistent with each other but sensitively different from Kozlov's values [22] reported in the last column of the table. Note that the comparison is somewhat unfair to Kozlov since the grid parameters used for the discrete representation of orbital wavefunctions have been adapted in both programs (RMS2 and MCDF-gme) to achieve a better accuracy.

3.3. Neutral lithium in the MCDHF approach

The MCDHF active space method consists in writing the total wavefunction as a CSF expansion built on a set of active one-electron orbitals. To investigate the convergence of the property, the orbital set is systematically expanded up to $n = 10$, but imposing the angular restriction $l_{\max} = 6$ (i orbitals). The sequence of CSFs active spaces (AS) is resumed as follows:

$\mathrm{AS}_0 = 1s^2 2s,$

$\mathrm{AS}_2 = \mathrm{AS}_0 + \{2p\},$

$\mathrm{AS}_3 = \mathrm{AS}_2 + \{3s, 3p, 3d\},$

$\mathrm{AS}_4 = \mathrm{AS}_3 + \{4s, 4p, 4d, 4f\},$

$\mathrm{AS}_5 = \mathrm{AS}_4 + \{5s, 5p, 5d, 5f, 5g\},$

$\mathrm{AS}_6 = \mathrm{AS}_5 + \{6s, 6p, 6d, 6f, 6g, 6h\},$

$\mathrm{AS}_7 = \mathrm{AS}_6 + \{7s, 7p, 7d, 7f, 7g, 7h, 7i\},$

$\mathrm{AS}_8 = \mathrm{AS}_7 + \{8s, 8p, 8d, 8f, 8g, 8h, 8i\},$

$\mathrm{AS}_9 = \mathrm{AS}_8 + \{9s, 9p, 9d, 9f, 9g, 9h, 9i\},$

$\mathrm{AS}_{10} = \mathrm{AS}_9 + \{10s, 10p, 10d, 10f, 10g, 10h, 10i\},$

where the (nl)-notation implies the relativistic shell structure $j = l \pm 1/2$. The configuration space is increased progressively by adding at each step a new layer of variational orbitals, keeping the previous ones frozen from the $(n-1)$ calculation. The MCDHF expansions are based on single and double (SD) excitations from the configuration reference.

Table 3. Contributions to the SMS K_{SMS} (in $m_e E_{\mathrm{h}}$) parameters for Li-like iron ($Z = 26$) and selenium ($Z = 34$) using unscreened Dirac one-electron wavefunctions.

	RMS2	MCDF-gme	Analytic	Kozlov [22]
Li-like iron		K^1_{SMS}		
$1s^2 2p_{1/2}\ {}^2P^o_{1/2}$	−55.247 250 67	−55.247 250 61	−55.247 250 683	−55.2474
$1s^2 2p_{3/2}\ {}^2P^o_{3/2}$	−53.264 431 37	−53.264 431 36	−53.264 431 362	−53.2645
		$K^2_{\mathrm{SMS}} + K^3_{\mathrm{SMS}}$		
$1s^2 2p_{1/2}\ {}^2P^o_{1/2}$	3.482 693 04	3.482 693 07	3.482 693 070	3.4278
$1s^2 2p_{3/2}\ {}^2P^o_{3/2}$	1.202 782 62	1.202 782 62	1.202 782 617	1.1960
Li-like selenium		K^1_{SMS}		
$1s^2 2p_{1/2}\ {}^2P^o_{1/2}$	−97.714 641 63	−97.714 641 40	−97.714 641 685	−97.7150
$1s^2 2p_{3/2}\ {}^2P^o_{3/2}$	−91.706 376 51	−91.706 376 51	−91.706 376 511	−91.7069
		$K^2_{\mathrm{SMS}} + K^3_{\mathrm{SMS}}$		
$1s^2 2p_{1/2}\ {}^2P^o_{1/2}$	10.538 847 31	10.538 8474	10.538 847 46	10.2546
$1s^2 2p_{3/2}\ {}^2P^o_{3/2}$	3.550 813 71	3.550 8137	3.550 813 72	3.5164

Table 4. Uncorrected (K^1_{NMS}) and corrected (K_{NMS}) NMS parameters (in $m_e E_{\mathrm{h}}$) for Li I.

	SD		SDT	
AS_n	K^1_{NMS}	K_{NMS}	K^1_{NMS}	K_{NMS}
	$1s^2 2s\ {}^2S_{1/2}$			
$n = 5$	7.479 955 285	7.473 188 966	7.480 387 512	7.473 620 714
$n = 6$	7.480 757 179	7.473 989 593	7.481 294 538	7.474 526 401
$n = 7$	7.480 843 823	7.474 076 167	7.481 413 156	7.474 644 913
$n = 8$	7.482 617 678	7.475 849 092	7.483 709 525	7.476 940 080
$n = 9$	7.482 764 972	7.475 996 085	7.483 865 298	7.477 095 534
$n = 10$	7.482 767 804	7.475 998 981	7.483 872 626	7.477 102 933
	$1s^2 2p\ {}^2P^o_{1/2}$			
$n = 5$	7.411 878 601	7.405 201 316	7.412 125 687	7.405 448 151
$n = 6$	7.412 307 495	7.405 629 843	7.412 599 631	7.405 921 698
$n = 7$	7.412 593 434	7.405 916 172	7.413 034 981	7.406 357 367
$n = 8$	7.414 193 990	7.407 516 244	7.415 203 718	7.408 525 555
$n = 9$	7.414 351 543	7.407 673 608	7.415 377 292	7.408 698 936
$n = 10$	7.414 365 017	7.407 687 009	7.415 402 512	7.408 724 081
	$1s^2 2p\ {}^2P^o_{3/2}$			
$n = 5$	7.411 871 260	7.405 208 436	7.412 118 064	7.405 455 006
$n = 6$	7.412 300 503	7.405 637 317	7.412 592 555	7.405 929 108
$n = 7$	7.412 584 979	7.405 922 413	7.413 026 010	7.406 363 146
$n = 8$	7.414 185 599	7.407 522 728	7.415 193 271	7.408 530 126
$n = 9$	7.414 343 399	7.407 680 348	7.415 366 987	7.408 703 663
$n = 10$	7.414 356 793	7.407 693 666	7.415 392 260	7.408 728 857

Triple excitations are investigated through SDT-configuration interaction (CI) calculations.

Tables 4 and 5 present the evolution of the NMS and the SMS parameter, respectively. In each table, both the uncorrected $\left(K^1_{\mathrm{MS}}\right)$ and corrected (K_{MS}) values are reported. Comparing the SD and SDT calculations, we observe that the influence of the triple excitations reaches more than 1% for the SMS while it is one order of magnitude smaller (0.1%) for the NMS.

In table 6, the individual contributions to the mass shift $\Delta\widetilde{K}_{\mathrm{MS}} (= \Delta K_{\mathrm{MS}}/h)$ parameters are reported for the $2p_{1/2}\ {}^2P^o_{1/2}$–$2s\ {}^2S_{1/2}$ (D_1 line) and $2p_{3/2}\ {}^2P^o_{3/2}$–$2s\ {}^2S_{1/2}$ (D_2 line) transitions in lithium. Values are calculated with the SD and SDT $n = 10$ active space final results of tables 4 and 5. Although many robust theoretical studies on the resonance line transition isotope shifts are available (see table 7 and the discussion below), the comparison with other theoretical works presented in table 6 is limited to the recent large-scale configuration-interaction Dirac–Fock–Sturm calculations of Kozhedub *et al* [26] since these authors precisely focus on the estimation of the relativistic nuclear recoil corrections. Kozhedub *et al*'s values are very consistent with our results: They report $\Delta\left(\widetilde{K}^2_{\mathrm{NMS}} + \widetilde{K}^3_{\mathrm{NMS}}\right) = 0.33$ and 0.38 GHz u for the D_1 and D_2 transitions, respectively. However, the uncorrected NMS contribution and therefore the total NMS values sensitively differ from each other by around 1.6 GHz u. This latter discrepancy is not understood yet and clearly deserves further investigations.

The uncorrected contribution of the SMS is also compared with the non-relativistic result of Godefroid *et al* [27] using the multiconfiguration Hartree–Fock method. More interesting is the comparison with the recent SMS values of Kozhedub *et al* [26] investigating the relativistic recoil corrections and using the same NMS and SMS partition according to (5) and

Table 5. Uncorrected ($K^1_{\rm SMS}$) and corrected ($K_{\rm SMS}$) SMS parameters (in $m_e E_{\rm h}$) for Li I.

	SD		SDT	
AS_n	$K^1_{\rm SMS}$	$K_{\rm SMS}$	$K^1_{\rm SMS}$	$K_{\rm SMS}$
	$1s^2 2s\ ^2S_{1/2}$			
$n=5$	0.301 034 3291	0.300 822 5633	0.301 376 7853	0.301 164 8528
$n=6$	0.301 036 1585	0.300 824 3666	0.301 457 9841	0.301 245 9847
$n=7$	0.301 954 4951	0.301 742 3943	0.302 439 6569	0.302 227 3237
$n=8$	0.301 861 7523	0.301 649 7153	0.302 411 5843	0.302 199 2791
$n=9$	0.301 798 7398	0.301 586 7742	0.302 351 2554	0.302 139 0203
$n=10$	0.301 856 1821	0.301 644 2119	0.302 414 1615	0.302 201 9200
	$1s^2 2p\ ^2P^o_{1/2}$			
$n=5$	0.248 934 2617	0.248 756 4343	0.249 060 4867	0.248 882 6064
$n=6$	0.248 288 1614	0.248 110 7089	0.248 428 2378	0.248 250 7247
$n=7$	0.248 299 3836	0.248 122 2326	0.248 410 7486	0.248 233 5819
$n=8$	0.247 601 5693	0.247 424 8242	0.247 455 7225	0.247 279 1143
$n=9$	0.247 520 7029	0.247 344 0589	0.247 371 9731	0.247 195 4806
$n=10$	0.247 656 6450	0.247 479 9659	0.247 513 1224	0.247 336 5865
	$1s^2 2p\ ^2P^o_{3/2}$			
$n=5$	0.248 933 1884	0.248 737 7216	0.249 059 2224	0.248 863 6586
$n=6$	0.248 289 2038	0.248 094 1432	0.248 428 9962	0.248 233 8261
$n=7$	0.248 302 2860	0.248 107 0388	0.248 413 9538	0.248 218 5782
$n=8$	0.247 603 9924	0.247 408 9620	0.247 458 5594	0.247 263 4414
$n=9$	0.247 523 3735	0.247 328 4034	0.247 375 0253	0.247 179 9634
$n=10$	0.247 660 6363	0.247 465 6360	0.247 517 6569	0.247 322 5644

Table 6. Individual contributions to the mass shift $\Delta\widetilde{K}_{\rm MS}$ (GHz u) parameters for the $2p\ ^2P^o_{1/2}$–$2s\ ^2S_{1/2}$ and $2p\ ^2P^o_{3/2}$–$2s\ ^2S_{1/2}$ transitions in lithium.

			$^2P^o_{1/2} - {}^2S_{1/2}$	$^2P^o_{3/2} - {}^2S_{1/2}$
NMS	$\Delta\widetilde{K}^1_{\rm NMS}$	SD	−246.899	−246.928
		SDT	−247.142	−247.179
	$\Delta\left(\widetilde{K}^2_{\rm NMS} + \widetilde{K}^3_{\rm NMS}\right)$	SD	0.328	0.382
		SDT	0.333	0.384
	$\Delta\widetilde{K}_{\rm NMS}$	SDT	−246.812	−246.795
	Other theory[a]		−245.15	−245.11
	Obs.[b]		−245.103	−245.108
SMS	$\Delta\widetilde{K}^1_{\rm SMS}$	SD	−195.632	−195.618
		SDT	−198.164	−198.148
	$\Delta(\widetilde{K}^2_{\rm SMS} + \widetilde{K}^3_{\rm SMS})$	SD	0.127	0.061
		SDT	0.129	0.062
	$\Delta\widetilde{K}_{\rm SMS}$	SDT	−198.035	−198.086
	Other theory[a]		−198.78	−198.77
	Other theory (NR)[c]		−198.66	−198.71
	Obs.[d]		−198.843	−198.101

[a] CI Dirac–Fock–Sturm calculation of Kozhedub *et al* [26].
[b] NMS values deduced from the transition frequencies [31] using (55) (see the text).
[c] Non-relativistic MCHF calculations [27].
[d] SMS values obtained by subtracting the 'observed' NMS (see footnote b above) from the IS measured by Das and Natarajan [31].

(6). As for the NMS, the relativistic corrections are in very nice agreement (they report $\Delta(\widetilde{K}^2_{\rm SMS} + \widetilde{K}^3_{\rm SMS}) = 0.12$ and 0.06 GHz u for the D_1 and D_2 lines) but the uncorrected forms do differ substantially with our estimation (they report for instance for the D_1 line, $\Delta\widetilde{K}^1_{\rm SMS} = -198.78$, against our value of −198.164 GHz u).

The comparison with observation for the individual mass contributions is also limited. There are a few reasons for this. First, as illustrated by (51), the FS contribution should be properly subtracted from the observed transition frequency before trying to extract the mass contribution. But this is usually the other way round that makes the theoretical calculation of mass shifts interesting: for a few-electron atomic systems like lithium indeed, the difference between the mass contribution calculated by elaborate *ab initio* calculations and the observed transition IS allows us to extract the change in the mean square charge radius of the nuclear charge distributions for all isotopes, as illustrated by the very recent and complete work of Nörtershäuser *et al* [28]. Another good reason is that once the FS 'eliminated', a clean separation of the NMS and SMS contributions could be criticized, as pointed out by Palmer [4]. However, remembering that for lithium, the FS is roughly 10^4 times smaller than the MS, it is worthwhile to neglect it for trying the mass separation exercise. There is indeed one experimental work by Radziemski *et al* [29] discussing the NMS and SMS separation in this line but as we will observe later (see table 7), the corresponding experimental transition IS values are not aligned with most of the other observed values. In their work, these authors separate the two mass shift contributions from the experimental transition IS in ^{6,7}Li, neglecting the FS contribution and approximating the Bohr mass shift by the experimental observed level energy, as suggested by Mårtensson and Salomonson [30]

$$\Delta^{\rm BMS} = -\frac{m_e}{M} E^B_M \simeq -\frac{m_e}{M} E_{\rm exp}. \tag{53}$$

From the same expression, we build the transition Bohr mass shift for the ^{6,7}Li isotope pair

$$\delta E_{\rm BMS} \simeq \left(\frac{m_e}{M(^6{\rm Li})} - \frac{m_e}{M(^7{\rm Li})}\right) \Delta E_{\rm exp} \tag{54}$$

Table 7. Mass shift $\Delta\widetilde{K}_{\rm MS}$ (GHz u) for the $2p_{1/2}\ ^2P^o_{1/2}$–$2s\ ^2S_{1/2}$ and $2p_{3/2}\ ^2P^o_{3/2}$–$2s\ ^2S_{1/2}$ transitions in Li I, compared with experimental IS.

	$^2P^o_{1/2}$–$^2S_{1/2}$	$^2P^o_{3/2}$–$^2S_{1/2}$	Ref.
$n = 9$	−445.1941	−445.2330	This work
$n = 10$	−444.8442	−444.8808	This work
Other theory	−447(12)	−447(12)	Korol and Kozlov [32]
	−443.81(20)	−443.82(20)	Kozhedub *et al* [26]
	−443.860 337 (253)	−443.876 984 (253)	Yan *et al* [33]
Experiment[a]	−443.89(3)	−443.91(2)	Sansonetti *et al* [34]
	−443.46(63)	−443.59(63)	Radziemski *et al* [29]
	−443.9033(63)	−443.9791(63)	Scherf *et al* [35]
	−443.9045(29)		Bushaw*et al* [36]
	−443.951(5)		Walls *et al* [37]
	−443.941(3)	−443.948(4)	Noble *et al* [38]
	−443.9490(16)	−443.9126(29)	Das and Natarajan [31]

[a] Inverting (52), i.e. using $\Delta\widetilde{K}_{\rm MS} = \delta\nu(M_1M_2)/(M_2 - M_1)$ (see the text).

from the observed transition energy. Combining (52) and (54), one finds

$$\Delta\widetilde{K}_{\rm NMS} \simeq m_e\frac{\Delta E_{\rm exp}}{h} = m_e\nu_{\rm exp} \tag{55}$$

from which we estimate the 'observed' NMS values reported in table 6, using the most recent absolute frequency measurements of Das and Natarajan [31]. The corresponding 'observed' $\Delta\widetilde{K}_{\rm SMS}$ values are calculated by subtracting the so-estimated NMS contribution from the experimental IS line shifts (−443.9490(16) GHz u and −443.9126(29) GHz u, for D_1 and D_2, respectively). Note that we did not take the liberty of reporting the frequency uncertainties estimated by Das and Natarajan on the separate contributions, the separability of NMS and SMS being by itself questionable.

Cleaner and in principle less problematic should be the comparison of the total mass shifts, as reported in table 7. On the theoretical side, we refer to the study of Korol and Kozlov [32] treating electron correlation with configuration interaction (CI) and many-body perturbation theory (MBPT) methods with Dirac–Fock orbitals to the calculations of Kozhedub *et al* [26] using the large-scale configuration-interaction Dirac–Fock–Sturm method and to the Yan *et al* [33] calculations estimating the mass corrections from highly correlated non-relativistic wavefunctions expressed in Hylleraas coordinates[8]. From all these elaborate results, we only kept the mass contributions, systematically excluding the contributions from the nuclear size corrections. We already noticed the differences between Kozhedub *et al*'s results and ours appearing in the separate NMS and SMS contributions. As commented above, these differences do not arise from the relativistic corrections ($K^2 + K^3$), but rather from the 'uncorrected' K^1 values, and should be further investigated. Our results seem to be of higher quality than the CI+MBPT results of Korol and Kozlov. As far as the differences with Yan *et al*'s results are concerned, we should keep in mind (i) that our orbital active set is truncated to $l_{\rm max} = 6$, (ii) that the layer approach adopted in the SD-MCDHF optimization could be a limiting factor and (iii) that the convergence of the $\Delta\widetilde{K}_{\rm MS}$ parameter as a function of the size of the active set is slow and not yet achieved at $n = 10$, as illustrated by the comparison of the two $n = 9$ and $n = 10$ sets of results reported in the table 7.

On the experimental side, we display in the same table 7, the experimental isotope shift values somewhat abusively converted in $\Delta\widetilde{K}_{\rm MS}$ parameters, i.e. neglecting the FS contribution and inverting (52), $\Delta\widetilde{K}_{\rm MS} = \delta\nu_k(M_1M_2)/(M_2 - M_1)$. As already mentioned, this conversion is unfair to physicists who devote much effort to extract the nuclear charge radii from the FS [28], but has the merit of illustrating where the present modest contribution lies in the distribution of experimental values. From this not exhaustive chronological list [29, 31, 34–38], it is clear that Radziemski *et al*'s results lie a bit outside the experimental distribution.

3.4. *B-like argon*

Large-scale calculations are performed for $1s^22s^22p\ ^2P^o_{1/2,3/2}$ of B-like argon ($Z = 18$). The radial orbital basis is obtained from SD-MCDHF calculations, including single and double excitations from all shells of the $\{1s^22s^22p, 1s^22p^3\}$ complex to increasing orbital active sets, up to the $\{10s9p8d7f6g3h1i\}$. Subsequently to this layer-by-layer SD-MCDHF orbital optimization, RCI calculations are performed including the Breit and QED effects in a space generated by SD excitations from the extended $\{1s^22s^22p, 1s^22p^3, 1s^22s2p3d, 1s^22p3d^2\}$ multireference set to the full orbital set. The expansion for the two J values includes more than 200 000 relativistic CSFs. This computational strategy has been developed by Rynkun *et al* [39] for the evaluation of transition rates in boron-like ions, from N III to Zn XXVI.

Table 8 illustrates the convergence of the NMS and SMS contributions with the increase of the active set. In table 9, the isotope shifts of the forbidden transitions $1s^22s^22p\ ^2P^o_{1/2}$–$^2P^o_{3/2}$ in ^{36,40}Ar are presented and compared with the mass shift results of Tupitsyn *et al* [8]. In their work, the CI Dirac–Fock method was used to solve the Dirac–Coulomb–Breit equation and to calculate the energies and the isotope shifts. The CSFs' expansions were generated including 'all single and

[8] The values of Yan *et al* reported in Kozhedub's paper [26] suggest that the atomic mass has been used in order to evaluate the mass shift parameter. In table 7, Yan *et al*'s values have been reevaluated using the nuclear mass.

Table 8. NMS and SMS parameters (in $m_e E_h$) values for the states $1s^2 2s^2 2p\ ^2P^o_{1/2}$ and $1s^2 2s^2 2p\ ^2P^o_{3/2}$ of B-like Ar.

AS_n	K^1_{NMS}	$\left(K^2_{NMS} + K^3_{NMS}\right)$	K^1_{SMS}	$\left(K^2_{SMS} + K^3_{SMS}\right)$
		$1s^2 2s^2 2p\ ^2P^o_{1/2}$		
$n = 3$	417.695 9959	−12.909 053 22	−16.149 602 37	0.469 056 12
$n = 4$	418.111 8745	−12.911 882 39	−16.308 959 58	0.477 634 19
$n = 5$	418.217 7551	−12.911 786 16	−16.337 597 42	0.478 898 11
$n = 6$	418.253 7558	−12.912 475 14	−16.324 036 19	0.475 808 53
$n = 7$	418.291 9516	−12.913 609 34	−16.344 903 31	0.476 588 69
$n = 8$	418.294 5374	−12.913 541 79	−16.342 598 43	0.476 123 08
$n = 9$	418.297 4119	−12.913 736 11	−16.343 557 66	0.476 210 31
$n = 10$	418.298 2181	−12.913 753 24	−16.343 524 53	0.476 096 22
$n = 10_{expand}$	418.299 5162	−12.913 789 55	−16.337 965 96	0.476 000 86
		$1s^2 2s^2 2p\ ^2P^o_{3/2}$		
$n = 3$	417.356 6053	−12.667 204 14	−15.914 698 60	0.128 215 57
$n = 4$	417.794 6482	−12.667 740 60	−16.090 169 93	0.134 646 20
$n = 5$	417.901 3634	−12.666 628 06	−16.115 109 03	0.133 357 29
$n = 6$	417.937 8902	−12.667 597 77	−16.101 421 89	0.131 284 56
$n = 7$	417.977 3669	−12.668 440 94	−16.122 553 33	0.131 351 16
$n = 8$	417.979 9742	−12.668 429 09	−16.120 029 82	0.131 048 64
$n = 9$	417.982 8424	−12.668 588 43	−16.120 978 00	0.131 042 62
$n = 10$	417.983 6553	−12.668 629 52	−16.120 943 41	0.131 002 31
$n = 10_{expand}$	417.984 6675	−12.668 657 88	−16.115 555 33	0.130 894 43

Table 9. Individual contributions to the wavenumber mass shift $\delta\sigma$ (cm^{-1}) for the forbidden transition $1s^2 2s^2 2p\ ^2P^o_{1/2}$–$^2P^o_{3/2}$ in boron-like ^{36,40}Ar.

	$\delta\sigma$				
	$\langle H^1_{NMS}\rangle$	$\langle H^2_{NMS} + H^3_{NMS}\rangle$	$\langle H^1_{SMS}\rangle$	$\langle H^2_{SMS} + H^3_{SMS}\rangle$	Total
This work	0.1054	−0.0821	−0.0745	0.1155	0.0644
Tupitsyn *et al* [8]	0.1053	−0.0822	−0.0742	0.1151	0.0640

double excitations and some part of triple excitations'. The nuclear charge distribution is described by a Fermi model and is therefore consistent with this work. For the purpose of our mass study, we deduced the FS from these and the Tupitsyn calculations.

Table 9 shows the individual contributions of operators (5) and (6) to the wavenumber mass shift. A good agreement is observed between the two sets of values, the total wavenumber mass shift values differing by less than 0.8%. This example beautifully confirms the importance of the relativistic corrections to the recoil operator: the total wavenumber mass shift would be indeed 50% smaller if estimated from the uncorrected form of the mass Hamiltonian $\langle H^1_{NMS} + H^1_{SMS}\rangle$.

Orts *et al* [40] succeeded to detect experimentally the IS of the transition with high precision and found a wonderful agreement with their theoretical predictions. The corresponding results are reported in table 10 and compared with our values. The nice agreement is a good sign of reliability for the tensorial form derivation of the nuclear recoil Hamiltonian of section 2.

3.5. C-like ions calculations

As another illustration of the importance of the relativistic corrections to the recoil operator, the values of the SMS, NMS and total level mass shift parameters are reported in table 11 for the levels arising from the ground configuration $1s^2 2s^2 2p^2$ in Ca XV and Sc XVI. As far as the calculations are concerned, the orbitals are obtained by SD-MCDHF calculations, considering single and double excitations from all shells of the $\{1s^2 2s^2 2p^2, 1s^2 2p^4\}$ Layzer's complex to the {8s7p6d5f4g2h} active set. These MCDHF calculations are followed by relativistic configuration interaction (RCI) calculations, including the Breit interaction and the QED corrections, using the enlarged multireference $\{1s^2 2s^2 2p^2, 1s^2 2p^4, 1s^2 2s 2p^2 3d, 1s^2 2s^2 3d^2\}$ set. The size of the expansions is around 350 000 relativistic CSFs. This computational method has been used by Jönsson *et al* [41] to calculate transition rates, hyperfine structures and Landé g factors for all carbon-like ions between F IV and Ni XXIII.

Table 10. Wavelength mass shift $\delta\lambda$ (nm, air) for the forbidden transition $1s^2 2s^2 2p\ ^2P^o_{1/2}$–$^2P^o_{3/2}$ in boron-like ^{36,40}Ar.

		λ (^{40}Ar)	$\delta\lambda$ (^{36,40}Ar)
This work		441.01	0.001 25
Orts *et al* [40]	Th.	441.16(27)	0.001 23(5)
	Obs.	441.2556(1)	0.001 23(6)

On the absolute scale of level shift parameters, one observes that the relativistic corrections $\left(K^2_{NMS} + K^3_{NMS}\right)$ to the NMS have the same order of magnitude than the uncorrected SMS contribution. Transition isotope shifts are

Table 11. SMS $K_{\rm SMS}$, NMS $K_{\rm NMS}$, total mass shifts $K_{\rm MS}$ parameters (all in $m_e E_{\rm h}$) for $2s^2 2p^2$ levels of Ca XV and Sc XVI from multireference RCI calculations. $K = K^1 + K^2 + K^3$.

		SMS		NMS		Total		
Level	J	$K^1_{\rm SMS}$	$K_{\rm SMS}$	$K^1_{\rm NMS}$	$K_{\rm NMS}$	$K^1_{\rm MS}$	$K_{\rm MS}$	$K^2_{\rm MS} + K^3_{\rm MS}$
				Ca XV				
$2s^2 2p^2\ ^3P$	0	−41.993	−40.659	558.358	538.033	516.364	497.374	−18.990
	1	−41.736	−40.741	558.070	537.983	516.334	497.242	−19.092
	2	−41.588	−40.821	557.854	537.929	516.266	497.108	−19.158
$2s^2 2p^2\ ^1D$	2	−41.451	−40.756	557.479	537.607	516.028	496.851	−19.177
$2s^2 2p^2\ ^1S$	0	−41.862	−41.199	557.000	537.200	515.138	496.001	−19.137
				Sc XVI				
$2s^2 2p^2\ ^3P$	0	−47.460	−45.771	621.221	596.303	573.761	550.532	−23.229
	1	−47.117	−45.874	620.842	596.236	573.725	550.362	−23.363
	2	−46.950	−45.964	620.592	596.169	573.642	549.219	−24.423
$2s^2 2p^2\ ^1D$	2	−46.765	−45.922	620.145	595.826	573.380	549.904	−23.476
$2s^2 2p^2\ ^1S$	0	−47.229	−46.421	619.624	595.390	572.395	548.969	−23.426

more interesting properties since they are the real observables if the resolution is good enough. These are monitored by the differential effects on the level IS. It is interesting to infer from table 11 the possible mass isotope shifts on the intraconfiguration (M1/E2) transition frequencies. Considering for example the Ca XV $^3P_1 \rightarrow {}^3P_2$ transition, the uncorrected total mass shift change is enlarged by a factor of 2 when including the $\left(K^2_{\rm MS} + K^3_{\rm MS}\right)$ relativistic corrections. For the $^3P_1 \rightarrow {}^1D_2$ transition, a similar increase of the mass shift is predicted but of 'only' 20%. Some reduction could occur: this is the case of $^3P_2 \rightarrow {}^1S_0$ (13%). For the $^3P_0 \rightarrow {}^1D_2$ transition, the relativistic recoil corrections reach 48%.

4. Conclusion and outlook

The irreducible tensorial form of the nuclear recoil Hamiltonian is derived in this work, opening interesting perspectives for calculating isotope shifts in the multiconfiguration Dirac–Hartree–Fock framework. We implemented the formalism in the relativistic package GRASP2K by writing a dedicated code (RMS2) for estimating the expectation values of the relativistic nuclear recoil operators. The comparison with other works is satisfactory and the results are promising, although not achieving the accuracy of the state-of-the-art methodology available for a few-electron systems. Electron correlation remains the major problem that might be solved in our schema with the use of the 'localized pair-correlation functions interaction method', as proposed by Verdebout *et al* [42]. This work enhances the fact that the relativistic corrections to the nuclear recoil are definitively necessary for obtaining reliable isotope shift calculations. The new computational tool, which we developed on the basis of the irreducible tensorial operator techniques, will hopefully provide valuable mass isotope shift data for large systems for which there are no reliable theoretical or experimental values.

Acknowledgments

CN is grateful to the 'Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture' of Belgium for a PhD grant (Boursier F.R.S.-FNRS). MRG and CN thank the Communauté française of Belgium (Action de Recherche Concertée) for financial support. MRG also acknowledges the Belgian National Fund for Scientific Research (FRFC/IISN Convention). Finally, the authors thank Jiguang Li for fruitful discussions.

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