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Tensorial form and matrix elements of the relativistic nuclear recoil operator

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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. The present work underlines the fact that the relativistic corrections to the nuclear recoil are definitively necessary for getting reliable isotope shift values.

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1. Introduction

Nuclear and relativistic effects in atomic spectra are treated in the pioneer 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 wave functions, 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 MCDHF-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 wave functions [14]. The tensorial form of the nuclear recoil Hamiltonian is derived in the present 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.

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

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 wave functions 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]

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

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

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

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 $\mathbf{r}^1 = r\mathbf{C}^1$, (3) becomes

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

with

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

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

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

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

and

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

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

2.1. Normal mass shift expectation value

The (mass-independent) normal mass shift parameter K_{NMS} is defined by the following expression

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

is found using

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

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

$$\begin{aligned} \langle n_a \kappa_a m_a | \frac{\mathbf{p}^2}{2} | n_b \kappa_b m_b \rangle &= \delta(\kappa_a m_a, \kappa_b m_b) \\ &\times \frac{1}{2} \int_0^\infty dr \left((\partial_r P_a) (\partial_r P_b) + (\partial_r Q_a) (\partial_r Q_b) + \frac{l_b(l_b+1) P_a P_b + \tilde{l}_b(\tilde{l}_b+1) Q_a Q_b}{r^2} \right), \end{aligned} \quad (17)$$

with $\tilde{l} = 2j - l$. 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

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

with

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

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

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

and

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

with $K = -(1 + \boldsymbol{\sigma} \cdot \mathbf{l})$, 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 wave function 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

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

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

$$\begin{aligned} [n_a \kappa_a || h_{\text{NMS}} || n_b \kappa_b] &= \delta(\kappa_a, \kappa_b) \\ &\times \frac{1}{2M} \int_0^\infty \left((\partial_r P_a) (\partial_r P_b) + (\partial_r Q_a) (\partial_r Q_b) + \frac{l_b(l_b+1)P_a P_b + \tilde{l}_b(\tilde{l}_b+1)Q_a Q_b}{r^2} \right. \\ &\left. + (-2\alpha Z) \frac{Q_a \partial_r P_b + Q_b \partial_r P_a}{r} + (-\alpha Z) \left(\frac{\kappa_b - 1}{r^2} \right) (Q_a P_b + Q_b P_a) \right) dr. \end{aligned} \quad (26)$$

2.2. Specific mass shift expectation value

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

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

and $K_{\text{SMS}}^1, K_{\text{SMS}}^2, K_{\text{SMS}}^3$ 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

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

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

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

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

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

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

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

where

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

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

$$X^1(abcd) = X_1^1(abcd) + X_2^1(abcd) + X_3^1(abcd) \quad (34)$$

that we analyzed hereafter separately.

2.2.1. First part: $X_1^1(abcd)$

Building $X_1^1(abcd)$ from (33), we have

$$g(r_i) \mathbf{T}^1(i) = \mathbf{p}^1(i) \quad ; \quad g(r_j) \mathbf{T}^1(j) = \mathbf{p}^1(j). \quad (35)$$

Introducing the one-electron reduced matrix element

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

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

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

the first contribution to the effective interaction strength writes as

$$X_1^1(abcd) = \langle \kappa_a \| \mathbf{C}^1 \| \kappa_c \rangle \langle \kappa_b \| \mathbf{C}^1 \| \kappa_d \rangle \mathcal{V}(n_a \kappa_a, n_c \kappa_c) \mathcal{V}(n_b \kappa_b, n_d \kappa_d), \quad (38)$$

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)

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

Introducing the matrix element

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

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

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

2.2.3. Third part: $X_3^1(abcd)$

Similarly, the two components of the third term of the SMS operator are

$$g(r_i)\mathbf{T}^1(i) = \frac{-\alpha Z}{r} (\sigma_x \otimes (\sigma_r(i)\mathbf{C}^1(i))) \quad ; \quad g(r_j)\mathbf{T}^1(j) = \mathbf{p}^1(j). \quad (42)$$

Using the matrix element

$$\begin{aligned} & \langle a | r^{-1} (\sigma_x \otimes (\sigma_r \mathbf{C}_q^1)) | c \rangle \\ &= i \int_0^\infty \frac{dr}{r} (Q_a P_c \langle -\kappa_a m_a | \mathbf{C}_q^1 | -\kappa_c m_c \rangle - Q_c P_a \langle \kappa_a m_a | \mathbf{C}_q^1 | \kappa_c m_c \rangle), \end{aligned} \quad (43)$$

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

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

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

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

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

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

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

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

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

3. Applications

We wrote a new program, hereafter referred as RMS2, for estimating the expectation values of the relativistic nuclear recoil operators using MCDHF wave functions 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 notice 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 $T_i = c \boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1) c^2$ associated to electron i , while the program RMS2 uses more accurately $\langle H_{\text{NMS}}^1 \rangle = \langle \sum_i p_i^2 / 2M \rangle$, which is consistent with section 2.1. An equivalent version has been written for the code MCDF-gme.

In the present 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:

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

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

$$B_{el}(Z) = 14.4381 Z^{2.39} + 1.55468 \cdot 10^{-6} Z^{5.35} . \quad (50)$$

The atomic and nuclear masses relevant to the present work are reported in Tables 1.

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
${}^6\text{Li}$	6.015122795(16)	6.01386737
${}^7\text{Li}$	7.01600455(8)	7.01474907
${}^{36}\text{Ar}$	35.967545106(29)	35.9576862
${}^{40}\text{Ar}$	39.9623831225(29)	39.9525242

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, $\delta\nu_k^{A_1,A_2} = (\delta E_j^{A_1,A_2} - \delta E_i^{A_1,A_2})/h$, 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 normal mass shift (NMS), specific mass shift (SMS) and field shift (FS) contributions :

$$\delta\nu_k^{A_1,A_2} = \underbrace{\delta\nu_{k,\text{NMS}}^{A_1,A_2} + \delta\nu_{k,\text{SMS}}^{A_1,A_2}}_{\delta\nu_{k,\text{MS}}^{A_1,A_2}} + \delta\nu_{k,\text{FS}}^{A_1,A_2}, \quad (51)$$

with

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

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 $\Delta \tilde{K}_{\text{MS}}[\text{GHz u}] = 3609.4824 \Delta K_{\text{MS}}[m_e E_h]$. 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 the 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 normal mass shift values calculated with the operators H_{NMS}^1 and $(H_{\text{NMS}}^2 + H_{\text{NMS}}^3)$, 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 wave functions [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 nonrelativistic and

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

|| The values reported in Tables 2 and 3 are based on $\alpha^{-1} = 137.035989500$ adopted in GRASP2K. For $1s_{1/2}$, the analytical result for K_{NMS} becomes 656.358886872 if adopting the $\alpha^{-1} = 137.035999679$ 2006 CODATA value [21].

relativistic recoil operators contain similar terms which, being rapidly growing when Z increases, cancel each other as discussed in [24] for Li-like ions.

Table 2. Contributions to the normal mass shift K_{NMS} parameters (in $m_e E_h$) for hydrogen-like selenium ($Z = 34$).

	RMS2	Kozlov [22]	Analytic
K_{NMS}^1			
$1s_{1/2}$	656.3589797	656.3589	656.358899684
$2p_{1/2}$	154.8937900	154.8938	154.893789883
$2p_{3/2}$	147.5192507	147.5192	147.519250700
$K_{\text{NMS}}^2 + K_{\text{NMS}}^3$			
$1s_{1/2}$	-78.3588949	-78.3589	-78.3588996839
$2p_{1/2}$	-8.0987869	-8.0988	-8.0987868710
$2p_{3/2}$	-3.0192507	-3.0193	-3.0192506997

3.2. Lithium-like systems using Dirac one-electron wave functions

The SMS parameters for Li-like iron ($Z = 26$) and selenium ($Z = 34$) are calculated in the single configuration approximation using three-electron wave functions 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 wave functions have been adapted in both programs (RMS2 and MCDF-gme) to achieve a better accuracy.

Table 3. Contributions to the specific mass shift K_{SMS} (in $m_e E_h$) parameters for Li-like iron ($Z = 26$) and selenium ($Z = 34$) using unscreened Dirac one-electron wave functions.

	RMS2	MCDF-gme	Analytic	Kozlov [22]
Li-like iron		K_{SMS}^1		
$1s^2 2p_{1/2} \ 2P_{1/2}^o$	-55.24725067	-55.24725061	-55.247250683	-55.2474
$1s^2 2p_{3/2} \ 2P_{3/2}^o$	-53.26443137	-53.26443136	-53.264431362	-53.2645
		$K_{\text{SMS}}^2 + K_{\text{SMS}}^3$		
$1s^2 2p_{1/2} \ 2P_{1/2}^o$	3.48269304	3.48269307	3.482693070	3.4278
$1s^2 2p_{3/2} \ 2P_{3/2}^o$	1.20278262	1.20278262	1.202782617	1.1960
Li-like selenium		K_{SMS}^1		
$1s^2 2p_{1/2} \ 2P_{1/2}^o$	-97.71464163	-97.71464140	-97.714641685	-97.7150
$1s^2 2p_{3/2} \ 2P_{3/2}^o$	-91.70637651	-91.70637651	-91.706376511	-91.7069
		$K_{\text{SMS}}^2 + K_{\text{SMS}}^3$		
$1s^2 2p_{1/2} \ 2P_{1/2}^o$	10.53884731	10.5388474	10.53884746	10.2546
$1s^2 2p_{3/2} \ 2P_{3/2}^o$	3.55081371	3.5508137	3.55081372	3.5164

3.3. Neutral lithium in the MCDHF approach

The MCDHF active space method consists in writing the total wavefunction as a configuration state function 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 $l_{\text{max}} = 6$ (i orbitals). The sequence of CSFs Active Spaces (AS) is resumed as follows

$$\begin{aligned}
 \text{AS}_0 &= 1s^2 2s, \\
 \text{AS}_2 &= \text{AS}_0 + \{2p\}, \\
 \text{AS}_3 &= \text{AS}_2 + \{3s, 3p, 3d\}, \\
 \text{AS}_4 &= \text{AS}_3 + \{4s, 4p, 4d, 4f\}, \\
 \text{AS}_5 &= \text{AS}_4 + \{5s, 5p, 5d, 5f, 5g\}, \\
 \text{AS}_6 &= \text{AS}_5 + \{6s, 6p, 6d, 6f, 6g, 6h\}, \\
 \text{AS}_7 &= \text{AS}_6 + \{7s, 7p, 7d, 7f, 7g, 7h, 7i\}, \\
 \text{AS}_8 &= \text{AS}_7 + \{8s, 8p, 8d, 8f, 8g, 8h, 8i\}, \\
 \text{AS}_9 &= \text{AS}_8 + \{9s, 9p, 9d, 9f, 9g, 9h, 9i\}, \\
 \text{AS}_{10} &= \text{AS}_9 + \{10s, 10p, 10d, 10f, 10g, 10h, 10i\},
 \end{aligned}$$

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

Table 4. Uncorrected (K_{NMS}^1) and corrected (K_{NMS}) normal mass shift parameters (in $m_e E_h$) for Li I.

AS_n	SD		SDT	
	K_{NMS}^1	K_{NMS}	K_{NMS}^1	K_{NMS}
	$1s^2 2s \ ^2S_{1/2}$			
$n=5$	7.479955285	7.473188966	7.480387512	7.473620714
$n=6$	7.480757179	7.473989593	7.481294538	7.474526401
$n=7$	7.480843823	7.474076167	7.481413156	7.474644913
$n=8$	7.482617678	7.475849092	7.483709525	7.476940080
$n=9$	7.482764972	7.475996085	7.483865298	7.477095534
$n=10$	7.482767804	7.475998981	7.483872626	7.477102933
	$1s^2 2p \ ^2P_{1/2}^o$			
$n=5$	7.411878601	7.405201316	7.412125687	7.405448151
$n=6$	7.412307495	7.405629843	7.412599631	7.405921698
$n=7$	7.412593434	7.405916172	7.413034981	7.406357367
$n=8$	7.414193990	7.407516244	7.415203718	7.408525555
$n=9$	7.414351543	7.407673608	7.415377292	7.408698936
$n=10$	7.414365017	7.407687009	7.415402512	7.408724081
	$1s^2 2p \ ^2P_{3/2}^o$			
$n=5$	7.411871260	7.405208436	7.412118064	7.405455006
$n=6$	7.412300503	7.405637317	7.412592555	7.405929108
$n=7$	7.412584979	7.405922413	7.413026010	7.406363146
$n=8$	7.414185599	7.407522728	7.415193271	7.408530126
$n=9$	7.414343399	7.407680348	7.415366987	7.408703663
$n=10$	7.414356793	7.407693666	7.415392260	7.408728857

Tables 4 and 5 present the evolution of the NMS and the SMS parameter, respectively. In each table both the uncorrected (K_{MS}^1) 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 $\Delta \tilde{K}_{\text{MS}} (= \Delta K_{\text{MS}}/h)$ parameters are reported for the $2p_{1/2} \ ^2P_{1/2}^o - 2s \ ^2S_{1/2}$ (D_1 line) and $2p_{3/2} \ ^2P_{3/2}^o - 2s \ ^2S_{1/2}$ (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 discussion below), the comparison with other theoretical works presented in Table 6 is

Table 5. Uncorrected (K_{SMS}^1) and corrected (K_{SMS}) specific mass shift parameters (in $m_e E_h$) for Li I.

AS_n	SD		SDT	
	K_{SMS}^1	K_{SMS}	K_{SMS}^1	K_{SMS}
	$1s^2 2s \ ^2S_{1/2}$			
$n=5$	0.3010343291	0.3008225633	0.3013767853	0.3011648528
$n=6$	0.3010361585	0.3008243666	0.3014579841	0.3012459847
$n=7$	0.3019544951	0.3017423943	0.3024396569	0.3022273237
$n=8$	0.3018617523	0.3016497153	0.3024115843	0.3021992791
$n=9$	0.3017987398	0.3015867742	0.3023512554	0.3021390203
$n=10$	0.3018561821	0.3016442119	0.3024141615	0.3022019200
	$1s^2 2p \ ^2P_{1/2}^o$			
$n=5$	0.2489342617	0.2487564343	0.2490604867	0.2488826064
$n=6$	0.2482881614	0.2481107089	0.2484282378	0.2482507247
$n=7$	0.2482993836	0.2481222326	0.2484107486	0.2482335819
$n=8$	0.2476015693	0.2474248242	0.2474557225	0.2472791143
$n=9$	0.2475207029	0.2473440589	0.2473719731	0.2471954806
$n=10$	0.2476566450	0.2474799659	0.2475131224	0.2473365865
	$1s^2 2p \ ^2P_{3/2}^o$			
$n=5$	0.2489331884	0.2487377216	0.2490592224	0.2488636586
$n=6$	0.2482892038	0.2480941432	0.2484289962	0.2482338261
$n=7$	0.2483022860	0.2481070388	0.2484139538	0.2482185782
$n=8$	0.2476039924	0.2474089620	0.2474585594	0.2472634414
$n=9$	0.2475233735	0.2473284034	0.2473750253	0.2471799634
$n=10$	0.2476606363	0.2474656360	0.2475176569	0.2473225644

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 $\Delta(\tilde{K}_{\text{NMS}}^2 + \tilde{K}_{\text{NMS}}^3) = 0.33$ 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 (6). As for the NMS, the relativistic corrections are in very nice agreement (they report $\Delta(\tilde{K}_{\text{SMS}}^2 + \tilde{K}_{\text{SMS}}^3) = 0.12$ 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, $\Delta\tilde{K}_{\text{SMS}}^1 = -198.78$, 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 field shift 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 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 $^{6,7}\text{Li}$, neglecting the field shift contribution and approximating the Bohr mass shift by the experimental observed level energy, as suggested by Mårtensson and Salomonson [30],

$$\Delta^{\text{BMS}} = -\frac{m_e}{M} E_M^B \simeq -\frac{m_e}{M} E_{exp}. \quad (53)$$

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

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

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

$$\Delta \tilde{K}_{\text{NMS}} \simeq m_e \frac{\Delta E_{exp}}{h} = m_e \nu_{exp} \quad (55)$$

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” $\Delta \tilde{K}_{\text{SMS}}$ 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 large-scale configuration-interaction Dirac-Fock-Sturm method and to the Yan *et al* [33] calculations estimating the mass

Table 6. Individual contributions to the mass shift $\Delta\tilde{K}_{\text{MS}}$ (GHz u) parameters for the $2p\ ^2P_{1/2}^o - 2s\ ^2S_{1/2}$ and $2p\ ^2P_{3/2}^o - 2s\ ^2S_{1/2}$ transitions in lithium

			$^2P_{1/2}^o - ^2S_{1/2}$	$^2P_{3/2}^o - ^2S_{1/2}$
NMS	$\Delta\tilde{K}_{\text{NMS}}^1$	SD	-246.899	-246.928
		SDT	-247.142	-247.179
	$\Delta(\tilde{K}_{\text{NMS}}^2 + \tilde{K}_{\text{NMS}}^3)$	SD	0.328	0.382
		SDT	0.333	0.384
	$\Delta\tilde{K}_{\text{NMS}}$	SDT	-246.812	-246.795
	Other theory ^a		-245.15	-245.11
Obs. ^b		-245.103	-245.108	
SMS	$\Delta\tilde{K}_{\text{SMS}}^1$	SD	-195.632	-195.618
		SDT	-198.164	-198.148
	$\Delta(\tilde{K}_{\text{SMS}}^2 + \tilde{K}_{\text{SMS}}^3)$	SD	0.127	0.061
		SDT	0.129	0.062
	$\Delta\tilde{K}_{\text{SMS}}$	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

^aCI Dirac-Fock-Sturm calculation of Kozhedub *et al* [26].

^bNMS values deduced from the transition frequencies [31] using (55) (see text).

^cNon-relativistic MCHF calculations [27].

^dSMS values obtained by subtracting the “observed” NMS (see footnote *b* above) from the IS measured by Das and Natarajan [31].

corrections from highly correlated non-relativistic wave functions expressed in Hylleraas coordinates[¶]. 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 values of Yan *et al* reported in the Kozhedub’s paper [26] suggest that the atomic mass has been used in order to evaluate the mass shift parameter. In table 7, the Yan *et al*’s values have been reevaluated using the nuclear mass.

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 $l_{max} = 6$, ii) that the layer approach adopted in the SD-MCDHF optimization could be a limiting factor and iii) that the convergence of the $\Delta\tilde{K}_{MS}$ 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 $\Delta\tilde{K}_{MS}$ parameters, ie. neglecting the FS contribution and inverting (52), $\Delta\tilde{K}_{MS} = \delta\nu_k(M_1M_2)/(M_2 - M_1)$. As already mentioned, this conversion is unfair to physicists who do some huge efforts 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 ([34, 29, 35, 36, 37, 38, 31]), it is clear that Radziemski *et al*'s results lie a bit outside the experimental distribution.

Table 7. Mass shift $\Delta\tilde{K}_{MS}$ (GHz u) for the $2p_{1/2} \ ^2P_{1/2}^o - 2s \ ^2S_{1/2}$ and $2p_{3/2} \ ^2P_{3/2}^o - 2s \ ^2S_{1/2}$ transitions in lithium, compared with experimental IS.

	$^2P_{1/2}^o - ^2S_{1/2}$	$^2P_{3/2}^o - ^2S_{1/2}$	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 <i>et al</i> [26]
	-443.860337(253)	-443.876984(253)	Yan <i>et al</i> [33]
Experiment ^a	-443.89(3)	-443.91(2)	Sansonetti <i>et al</i> [34]
	-443.46(63)	-443.59(63)	Radziemski <i>et al</i> [29]
	-443.9033(63)	-443.9791(63)	Scherf <i>et al</i> [35]
	-443.9045(29)		Bushaw <i>et al</i> [36]
	-443.951(5)		Walls <i>et al</i> [37]
	-443.941(3)	-443.948(4)	Noble <i>et al</i> [38]
	-443.9490(16)	-443.9126(29)	Das and Natarajan [31]

^a inverting (52), ie. using $\Delta\tilde{K}_{MS} = \delta\nu(M_1M_2)/(M_2 - M_1)$ (see text)

3.4. B-like argon

Large-scale calculations are performed for $1s^22s^22p \ ^2P_{1/2,3/2}^o$ 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 increasing of the active set. In Table 9, the isotope shifts of the forbidden transitions

Table 8. NMS and SMS parameters (in $m_e E_h$) values for the states $1s^22s^22p \ ^2P_{1/2}^o$ and $1s^22s^2 2p \ ^2P_{3/2}^o$ states of B-like Ar.

AS_n	K_{NMS}^1	$(K_{\text{NMS}}^2 + K_{\text{NMS}}^3)$	K_{SMS}^1	$(K_{\text{SMS}}^2 + K_{\text{SMS}}^3)$
$1s^22s^22p \ ^2P_{1/2}^o$				
$n = 3$	417.6959959	-12.90905322	-16.14960237	0.46905612
$n = 4$	418.1118745	-12.91188239	-16.30895958	0.47763419
$n = 5$	418.2177551	-12.91178616	-16.33759742	0.47889811
$n = 6$	418.2537558	-12.91247514	-16.32403619	0.47580853
$n = 7$	418.2919516	-12.91360934	-16.34490331	0.47658869
$n = 8$	418.2945374	-12.91354179	-16.34259843	0.47612308
$n = 9$	418.2974119	-12.91373611	-16.34355766	0.47621031
$n = 10$	418.2982181	-12.91375324	-16.34352453	0.47609622
$n = 10_{\text{expand}}$	418.2995162	-12.91378955	-16.33796596	0.47600086
$1s^22s^22p \ ^2P_{3/2}^o$				
$n = 3$	417.3566053	-12.66720414	-15.91469860	0.12821557
$n = 4$	417.7946482	-12.66774060	-16.09016993	0.13464620
$n = 5$	417.9013634	-12.66662806	-16.11510903	0.13335729
$n = 6$	417.9378902	-12.66759777	-16.10142189	0.13128456
$n = 7$	417.9773669	-12.66844094	-16.12255333	0.13135116
$n = 8$	417.9799742	-12.66842909	-16.12002982	0.13104864
$n = 9$	417.9828424	-12.66858843	-16.12097800	0.13104262
$n = 10$	417.9836553	-12.66862952	-16.12094341	0.13100231
$n = 10_{\text{expand}}$	417.9846675	-12.66865788	-16.11555533	0.13089443

$1s^22s^22p \ ^2P_{1/2}^o - ^2P_{3/2}^o$ in $^{36,40}\text{Ar}$ 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 double excitations and some part of triple excitations”. The nuclear charge distribution is described by a Fermi

model and is therefore consistent with the present work. For the purpose of our mass study, we deduced the field shift 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 $\langle H_{\text{NMS}}^1 + H_{\text{SMS}}^1 \rangle$.

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.

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

	$\delta\sigma$				Total
	$\langle H_{\text{NMS}}^1 \rangle$	$\langle H_{\text{NMS}}^2 + H_{\text{NMS}}^3 \rangle$	$\langle H_{\text{SMS}}^1 \rangle$	$\langle H_{\text{SMS}}^2 + H_{\text{SMS}}^3 \rangle$	
This work	0.1054	-0.0821	-0.0745	0.1155	0.0644
Tupitsyn <i>et al</i> [8]	0.1053	-0.0822	-0.0742	0.1151	0.0640

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

	λ (^{40}Ar)	$\delta\lambda$ ($^{36,40}\text{Ar}$)
This work	441.01	0.00125
Orts <i>et al</i> [40]	th. 441.16(27)	0.00123(5)
	obs. 441.2556(1)	0.00123(6)

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 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.

On the absolute scale of level shift parameters, one observes that the relativistic corrections ($K_{\text{NMS}}^2 + K_{\text{NMS}}^3$) to the NMS have the same order of magnitude than the uncorrected SMS contribution. Transition isotope shifts are 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 two when including the ($K_{\text{MS}}^2 + K_{\text{MS}}^3$) 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 the present 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 “localized pair-correlation functions interaction method”, as proposed by Verdebout *et al* [42]. The present work enhances the fact that the relativistic corrections to the nuclear recoil are definitively necessary for getting reliable isotope shift calculations. The new computational tool, that 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

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

Level	J	SMS		NMS		Total		
		K_{SMS}^1	K_{SMS}	K_{NMS}^1	K_{NMS}	K_{MS}^1	K_{MS}	$K_{\text{MS}}^2 + K_{\text{MS}}^3$
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

values.

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References

- [1] A.P. Stone. *Proc. Phys. Soc.*, 77:786, 1961.
- [2] A.P. Stone. *Proc. Phys. Soc.*, 81:868, 1963.
- [3] L. Veseth. *J. Phys. B : At. Mol. Phys.*, 18:3463–3480, 1985.
- [4] C.W.P. Palmer. *J. Phys. B : At. Mol. Phys.*, 20:5987–5996, 1987.
- [5] F.A. Parpia, M. Tong, and C. Froese Fischer. *Phys. Rev. A*, 46:3717–24, 1992.
- [6] P. Jönsson and C. Froese Fischer. *Comput. Phys. Commun.*, 100:81–92, 1997.
- [7] V.M. Shabaev and A.N. Artemyev. *J. Phys. B : At. Mol. Phys.*, 27:1307–1314, 1994.
- [8] I. I. Tupitsyn, V. M. Shabaev, J. R. Crespo López-Urrutia, I. Draganic, R. Soria Orts, and J. Ullrich. *Phys. Rev. A*, 68:022511, 2003.
- [9] S. G. Porsev, M. G. Kozlov, and D. Reimers. *Phys. Rev. A*, 79(3):032519, 2009.
- [10] P. Jönsson, X. He, C. Froese Fischer, and I.P. Grant. *Comput. Phys. Commun.*, 177:597–622, 2007.
- [11] P. Indelicato and J.P. Desclaux. Mcdfgme, a multiconfiguration dirac-fock and general matrix elements program, release 2008, <http://dirac.spectro.jussieu.fr/mcdf>. 2008.
- [12] J.P. Desclaux. In E. Clementi, editor, *Methods and Techniques in Computational Chemistry - vol. A: Small Systems of METTEC*, page 253. Cagliari, 1993.
- [13] G. Gaigalas, S. Fritzsche, and I.P. Grant. *Comput. Phys. Commun.*, 139:263–278, 2001.
- [14] I.P. Grant. *Relativistic Quantum Theory of Atoms and Molecules. Theory and Computation.* Atomic, Optical and Plasma Physics. Springer, New York, USA, 2007.
- [15] R. D. Cowan. *The Theory of Atomic Structure and Spectra.* Los Alamos Series in Basic and Applied Sciences. University of California Press, 1981.
- [16] G. Gaigalas, Z. Rudzikas, and C. Froese Fischer. *J. Phys. B : At. Mol. Phys.*, 30:3747–71, 1997.
- [17] E.P. Wigner. *Group Theory and its Applications to the Quantum Mechanics of Atomic Spectra.* Academic Press, New York, 1959.
- [18] K.-N. Huang, M. Aoyagi, M.H. Chen, B. Crasemann, and H. Mark. *At. Data Nucl. Data Tables*, 18:243–291, 1976.
- [19] D. Lunney, J. M. Pearson, and C. Thibault. *Rev. Mod. Physics*, 75(3):1021, 2003.
- [20] J.S. Coursey, D.J. Schwab, J.J. Tsai, and R.A. Dragoset, 2010. Atomic Weights and Isotopic Compositions (version 3.0). [Online] Available: <http://physics.nist.gov/Comp> [2010, 11 27]. National Institute of Standards and Technology, Gaithersburg, MD.
- [21] P.J. Mohr, B.N. Taylor, and D.B. Newell. *Rev. Mod. Physics*, 80:633.
- [22] M. G. Kozlov. http://qchem.pnpi.spb.ru/kozlov/m/my_papers/notes/sms_rel.pdf, October 2010.
- [23] W. R. Johnson. *Atomic Structure Theory: Lectures on Atomic Physics.* Springer Verlag, Berlin, Heidelberg, Springer-Verlag edition, 2007.
- [24] A.N. Artemyev, V.M. Shabaev, and V.A. Yerokhin. *Phys. Rev. A*, 52:1884, 1995.
- [25] C. Nazé, M. Godefroid, J.-P. Desclaux, and P. Indelicato. 2011. (work in progress).
- [26] Y. S. Kozhedub, A. V. Volotka, A. N. Artemyev, D. A. Glazov, G. Plunien, V. M. Shabaev, I. I. Tupitsyn, and Th. Stöhlker. *Phys. Rev. A*, 81(4):042513, Apr 2010.
- [27] M. Godefroid, C. Froese Fischer, and P. Jönsson. *J. Phys. B : At. Mol. Phys.*, 34:1079–1104, 2001.
- [28] W. Nörtershäuser, R. Sánchez, G. Ewald, A. Dax, J. Behr, P. Bricault, B. A. Bushaw, J. Dilling, M. Dombisky, G. W. F. Drake, S. Götze, H.-J. Kluge, Th. Kühl, J. Lassen, C. D. P. Levy, K. Pachucki, M. Pearson, M. Puchalski, A. Wojtaszek, Z.-C. Yan, and C. Zimmermann. *Phys. Rev. A*, 83(1):012516, Jan 2011.
- [29] L. J. Radziemski, R. Engleman, and J. W. Brault. *Phys. Rev. A*, 52(6):4462–4470, Dec 1995.
- [30] A.-M. Mårtensson and S. Salomonson. *J. Phys. B : At. Mol. Phys.*, 15:2115–2130, 1982.
- [31] D. Das and V. Natarajan. *Phys. Rev. A*, 75(5):052508, May 2007.
- [32] V. A. Korol and M. G. Kozlov. *Phys. Rev. A*, 76(2):022103–7, 2007.
- [33] Z.-C. Yan, W. Nörtershäuser, and G.W.F. Drake. *Phys. Rev. Lett.*, 100:243002, 2008.
- [34] C. J. Sansonetti, B. Richou, R. Engleman, and L. J. Radziemski. *Phys. Rev. A*, 52(4):2682–2688,

Oct 1995.

- [35] W. Scherf, O. Khait, H. Jäger, and L. Windholz. *Z. Phys.D–Atoms, Molecules and Clusters*, 36:31–33, 1996.
- [36] B. A. Bushaw, W. Nörtershäuser, G. Ewald, A. Dax, and G. W. F. Drake. *Phys. Rev. Lett.*, 91(4):043004, Jul 2003.
- [37] J. Walls, R. Ashby, J. J. Clarke, B. Lu, and W. A. Van Wijngaarden. *Eur. Phys. J. D*, 22(2):159–162, 2003.
- [38] G. A. Noble, B. E. Schultz, H. Ming, and W. A. van Wijngaarden. *Phys. Rev. A*, 74(1):012502, Jul 2006.
- [39] P. Rynkun, P. Jönsson, G. Gaigalas, and C. Froese Fischer. *At. Data Nucl. Data Tables*, 2011. in press.
- [40] R. Soria Orts, Z. Harman, J. R. Crespo Lopez-Urrutia, A. N. Artemyev, H. Bruhns, A. J. Gonzalez Martinez, U. D. Jentschura, C. H. Keitel, A. Lapierre, V. Mironov, V. M. Shabaev, H. Tawara, I. I. Tupitsyn, J. Ullrich, and A. V. Volotka. *Phys. Rev. Lett.*, 97(10):103002, 2006.
- [41] P. Jönsson, P. Rynkun, and G. Gaigalas. *At. Data Nucl. Data Tables*, 2011. accepted.
- [42] S. Verdebout, P. Jönsson, G. Gaigalas, M. Godefroid, and C. Froese Fischer. *J. Phys. B : At. Mol. Phys.*, 43:074017, 2010.