Signs in isotope shifts: a perennial headache

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Signs of the different contributions to the isotope shift of an atomic line are discussed in details
to clarify some confusing differences between the electronic parameters calculated with RIS [1, 2]
and those appearing in other commonly used expressions.

I. RIS3 AND RIS4 SIGN CONVENTIONS

The sign conventions used in the description of the iso-
topic shift RIS3 [1] and RIS4 [2] of the GRASP package [3]
are explained in details in section 3 of Ekman et al. [2].
When evaluating the frequency isotope shift \( \delta \nu_{k,IS} \) of a
given spectral line \( k \) from the relevant electronic and nu-
clear factors, one should pay attention to the definition of
the frequency isotope shift itself. The latter is defined in RIS [1, 2] as

\[
[\delta \nu_{k,IS}^{A,A'}]_{\text{RIS}} = \nu_k^A - \nu_k^{A'},
\]

(1)

with the convention \( A > A' \), while in many other works [4–6], it is defined the other way round, as in the
original work compilation of Heilig and Steudel (HS) [7],
i.e.

\[
[\delta \nu_{k,IS}^{A,A'}]_{\text{HS}} = \nu_k^{A'} - \nu_k^A = -[\delta \nu_{k,IS}^{A,A'}]_{\text{RIS}},
\]

(2)

with the convention \( A' > A \). These two different conventions, \( A > A' \) for RIS, and \( A' > A \) for HS, restore the sign compatibility for the isotope shifts of a spectral line calculated with both definitions, (1) and (2). According

to Heilig and Steudel [7] or Bauche and Champeau [8]
indeed, the isotope shift of a spectral line is called pos-
itive when the heavier isotope is shifted towards larger
wavenumbers, i.e. \( \nu_k^A > \nu_k^{A'} \) when \( A' > A \). Keeping the
same convention for a positive frequency IS requires the condition \( A > A' \) if adopting the RIS definition (1). Such
positive isotope shifts correspond to the following cases

\[
[\delta \nu_{k,IS}^{A,A'}]_{\text{HS}} = -[\delta \nu_{k,IS}^{A',A}]_{\text{HS}}
\]

\[
= -[\delta \nu_{k,IS}^{A,A'}]_{\text{RIS}} = +[\delta \nu_{k,IS}^{A',A}]_{\text{RIS}} > 0 \quad (A' > A) \quad (3)
\]

\[
< 0 \quad (A' < A) \quad (4)
\]

that can be resumed in the following table:

| \( A' > A \) | \( \delta \nu_{k,IS}^{A,A'} \)_{\text{HS}} | \( \delta \nu_{k,IS}^{A,A'} \)_{\text{RIS}} |
|--------------|----------------|----------------|
| > 0          | > 0            | < 0            |
| < 0          | 0              | 0              |

taking the \( A \leftrightarrow A' \) permutation property \( \delta \nu^{A',A} = -\delta \nu^{A',A} \) into account.

Note that the RIS definition (1) is consistent with
previous works [9–13] defining the isotope shift on the
electron-affinity

\[
\text{IS}(A, A') = \delta \epsilon A = \epsilon A(A) - \epsilon A(A').
\]

(5)
as being positive for \( A' < A \).

A. Mass shift

The total mass shift is often written as [5]

\[
[\delta \nu_{k,MS}^{A,A'}]_{\text{HS}} = M_k \frac{A' - A}{AA'} , \quad (6)
\]

while RIS defines it as

\[
[\delta \nu_{k,MS}^{A,A'}]_{\text{RIS}} = \left( \frac{M' - M}{MM'} \right) \frac{\Delta K_{MS}}{h} = \left( \frac{M' - M}{MM'} \right) \Delta K_{MS} . \quad (7)
\]

The mass factor having the same sign in both (6) and
(7), the sign difference (2) forces us to accept that

\[
\Delta K_{MS} = -M_k . \quad (8)
\]

If the normal mass shift (NMS) is the only contribution to
the mass isotope shift, the latter is necessarily positive, corresponding to a “normal” isotope shift when referring
to the mass IS of lines in hydrogen-like (single-electron)
system. In that case, we have

\[
M_k > 0 , \quad (9)
\]

\[
\Delta K_{MS} < 0 . \quad (10)
\]

For many-electron systems, the specific mass shift (SMS)
due to the mass polarization term can counter-balance
the normal mass shift (NMS). It can be even large enough
to produce an “anomalous” mass isotope shift [9, 12], cor-
responding to a smaller frequency for the heavier isotope.

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B. Field shift

The field shift (FS) is expressed in RIS as

\[
[\delta \nu_{IS}^{A,A'}]_{\text{RIS}} = F_k \left[ \delta \langle r^2 \rangle^{A,A'} \right]_{\text{RIS}}
\]

with

\[
[\delta \langle r^2 \rangle^{A,A'}]_{\text{RIS}} = \langle r^2 \rangle^A - \langle r^2 \rangle^{A'}. \tag{12}
\]

Unfortunately, the sign of the change in the root-mean-square nuclear charge radii (12) also differs with other (commonly used) conventions [4–7]

\[
[\delta \langle r^2 \rangle^{A,A'}]_{\text{RIS}} = -[\delta \langle r^2 \rangle^{A,A'}]_{\text{HS}}. \tag{13}
\]

C. Total isotope shift

Adding the mass shift (7) and the field shift (11), the total isotope shift calculated with the RIS codes writes as

\[
[\delta \nu_{IS}^{A,A'}]_{\text{RIS}} = \left( \frac{M' - M}{MM'} \right) [\Delta K_{MS}]_{\text{RIS}} + F \left[ \delta \langle r^2 \rangle^{A,A'} \right]_{\text{RIS}}. \tag{14}
\]

Applications of (14) can be found in the multiconfiguration Dirac-Hartree-Fock calculations of electronic isotope shift factors in Li-like ions [14], Be-like ions [15], Ba I [16], Mg I [17], Al I [18], Zn I [19], Sh I [20], Os I [21], Ir I [22], and of In²⁺, In I, Ti²⁺ and Ti I [13], using the auxiliary computational tool fical included in the GRASP package.

Due to the sign differences (8) and (13), this last expression differs from Cheal et al. [5] (CCF)

\[
[\delta \nu_{IS}^{A,A'}]_{\text{CCF}} = \left( \frac{A' - A}{AA'} \right) [M]_{\text{CCF}} + F \left[ \delta \langle r^2 \rangle^{A,A'} \right]_{\text{CCF}} \tag{15}
\]

or from Blum et al. [6] (BDN)

\[
[\delta \nu_{IS}^{A,A'}]_{\text{BDN}} = \left( \frac{M_A' - M_A}{M_AM_A'} \right) [K_{MS}]_{\text{BDN}} + F \left[ \delta \langle r^2 \rangle^{A,A'} \right]_{\text{BDN}} \tag{16}
\]

who adopt the Heilig and Steudel definition of \( \delta \langle r^2 \rangle^{A,A'} \)

\( \delta \langle r^2 \rangle^{A,A'}_{\text{RIS}} = \langle r^2 \rangle^{A'} - \langle r^2 \rangle^{A} \). Comparing (14) with (15) or (16), and taking into account that

\[
[\delta \nu_{IS}^{A,A'}]_{\text{RIS}} = -[\delta \nu_{IS}^{A,A'}]_{\text{CCF}} = -[\delta \nu_{IS}^{A,A'}]_{\text{BDN}}, \tag{17}
\]

one deduces that the field shift factor \( F \) is the same for all conventions while

\[
[\Delta K_{MS}]_{\text{RIS}} = -[M]_{\text{CCF}} = -[K_{MS}]_{\text{BDN}}. \tag{18}
\]

The \textit{ab initio} calculated electronic mass parameters, \( [\Delta K_{MS}]_{\text{RIS}} \), had therefore to be sign-inverted according to (18) to be properly treated in experimental studies adopting (15) or (16) expressions [23–25].

II. RECOMMENDATIONS

To avoid misinterpretation or misuse of the electronic parameters estimated with atomic structure codes, it is highly recommended to emphasize the possibility of sign conflict between the different conventions. The minimal recommendation is to refer to the appropriate isotope shift expression, (14), (15) or (16), with the relevant crucial sign conventions (1) or (2) used for \( \delta \nu_{IS}^{A,A'} \) and \( \delta \langle r^2 \rangle^{A,A'} \).

III. HELPFUL CONSIDERATIONS

For the FS contribution, we should keep in mind that:

1. Deeper is the potential, more bound are the electronic levels.

2. The finite volume effect eliminates the singularity of the point-charge nucleus model and therefore decreases the binding energy.

3. This reduction of the binding energy increases with the electron density at the nucleus. Therefore, for a given isotope, omitting the mass shift, the frequency of a line (always positive) is smaller for a finite nuclear charge than for a point-charge nucleus if the electronic density at the nucleus is smaller for the upper level than for the lower level,

(b) larger for a finite nuclear charge than for a point-charge nucleus if the electronic density at the nucleus is larger for the upper level than for the lower level.

4. For a given isotope pair and a given electronic transition, we should consider the sign of \( \delta \langle r^2 \rangle \) when comparing the effect of the finite nuclear charge distribution between the two isotopes. Referring to the above terminology, we can qualify the frequency shift due to the volume effect as a “normal” or “anomalous” field shift:

(a) if the heaviest isotope has a larger nuclear volume than the lightest isotope, (increasing of the nuclear radius with the number of nucleons),

i. the line frequency will be \textit{smaller} for the heaviest isotope if we are in case 4(a) (decreasing of the electron density when exciting the atom) i.e., anomalous FS.

ii. the line frequency will be \textit{larger} for the heaviest isotope if we are in case 4(b) (increasing of the electron density when exciting the atom) i.e., normal FS.
(b) if the heaviest isotope has a smaller nuclear volume than the lightest isotope, (decreasing of the nuclear radius with the number of nucleons),

i. the line frequency will be larger for the heaviest isotope if we are in case 4(a) (decreasing of the electron density when exciting the atom) i.e., normal FS.

ii. the line frequency will be smaller for the heaviest isotope if we are in case 4(b) (increasing of the electron density when exciting the atom) i.e., anomalous FS.

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