Isotope shift on the chlorine electron affinity revisited by an MCHF/CI approach

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Abstract

Today, the electron affinity is experimentally well known for most of the elements and is a useful guideline for developing \textit{ab initio} computational methods. However, the measurements of isotope shifts on the electron affinity are limited by both resolution and sensitivity. In this context, theory is of great help to further our knowledge and understanding of atomic structures, even though correlation plays a dominant role in negative ions’ properties and, particularly, in the calculation of the specific mass shift contribution. This study solves the longstanding discrepancy between calculated and measured specific mass shifts on the electron affinity of chlorine (Berzinsh \textit{et al} 1995 \textit{Phys. Rev.} A \textbf{51} 231).

(Some figures may appear in colour only in the online journal)

1. Introduction

Despite the difficulty in measuring electron affinities (\(\varepsilon A\)), experimental values can be considered ‘exact’ by theoreticians for most of the elements. Due to their remarkable properties as weakly bound atomic systems largely governed by electron correlation, negative ions have always attracted broad attention from chemists and atomic physicists [1]. In this respect, the field of electron affinities constitutes a playground of choices for testing the computational methods, see e.g. [2, 3]. The estimation of the mass polarization operator expectation value that partly makes the level isotope shift (IS), also highly sensitive to correlation [4], offers other stringent tests of the reliability of theoretical methods. Unfortunately, the mass shifts (MSs) of transition frequencies or electron detachment thresholds are rather difficult to extract from experimental studies. Limitations arise from the size of ISs and/or from the low abundances of the isotopes to be studied, in which cases isotopically enriched samples [5] or in-source spectroscopy [6] could be used. One way of deducing a pure MS value from observation is the use of King plots [7, 8], requiring the measurements of ISs on two transitions for at least two pairs of isotopes. Due to the nuclear stability valley narrowing for low atomic numbers, there are fewer possibilities of building the required experimental King plots when approaching the domain of systems for which it is realistic to perform highly correlated calculations. Any other way of estimating the field shift (FS) and MS contributions separately must contain theoretical inputs [9, 10]. In cases where either the FS or MS is a small contribution, the error on the theoretical part is often neglected, although it involves in some cases an unknown systematic error in the data analysis [11].

In the context of the physics of highly charged ions, the balance between the MS and FS contributions to the level and transition ISs is worthwhile to investigate systematically along an isoelectronic sequence [12] for which the increasing importance of a proper relativistic treatment towards the high-Z region becomes obvious [13–16]. However, for the study of the ISs on the electronic structure of negative and neutral atoms of the second and third periods of the periodic table, electron correlation still largely dominates the relativistic corrections, and non-relativistic approaches constitute a good starting point to investigate what makes an IS ‘normal’ or ‘anomalous’ [17, 18].
In the field of negative ions, the laser photodetachment threshold technique was developed and successfully applied to the measurement of electron affinities [19] and of the detachment thresholds corresponding to different fine-structure levels of the negative ion and the neutral atom [20, 21]. In this method, the onset of the photodetachment process is measured directly using a tunable laser source. In combination with improved methods for the measurement of the photoelectron kinetic energies such as photodetachment microscopy [22] and slow-electron velocity-map imaging [23], the technique of laser photodetachment at the threshold represents the most precise way of determining photodetachment thresholds experimentally [24]. Amongst the recent applications of photodetachment microscopy, let us cite the first experiment realized in phosphorus with the excitation of the parent neutral atom out of the fundamental spectral term [25] and the measurement of the electron affinity of selenium with an accuracy of 1 μeV [26]. The possibility of applying the tunable laser photodetachment spectroscopy to the measurement of the IS on the electron affinity was demonstrated for the first time by Berzinsh et al. [27] for the 35,37Cl isotopes. The photodetachment microscopy technique was applied later to measure the electron affinities of 16O and 18O separately from a natural sample [28] and deduce the IS on the oxygen electron affinities for 16,18O. This work was extended to 17O [29] with the assistance of theoretical calculations for the estimation of the hyperfine structures. The sulfur electron affinities were measured more recently by photodetachment microscopy for the two isotopes 32S and 34S [30], demonstrating the ability of ab initio methods for estimating the IS on the electron affinity.

More than 15 years ago, measurements and many-body calculations were reported for the IS in the chlorine electron affinity in the pioneering work of Berzinsh et al. [27]. The theory–experiment agreement found for the specific mass shift (SMS) and FS contributions was satisfactory as far as the order of magnitude is concerned but a serious discrepancy lay in its sign. Still, the resolution obtained by tunable-laser photodetachment spectroscopy was remarkable. More recently, the IS on the electron affinity of sulfur was investigated, both experimentally and theoretically [30]. It was established that large-scale closed-core multiconfiguration Hartree–Fock (MCHF) calculations lead to a reasonable theory–experiment agreement, but it was also shown that the core effects are large and cannot be neglected. The success found in [30] for the S/S systems incited the present authors to revisit theoretically the IS on the electron affinity (ΔA) of chlorine, involving only one more electron in the neutral/negative ion balance. Section 2 presents the needed theoretical background, introducing the mass and field IS on the electron affinity. The correlation models and construction of the configuration spaces are described in section 3. Sections 4.1 and 4.2 present, respectively, the results of the valence correlation models and that of the open-core configuration interaction (CI) approach. The final theoretical results are summarized and compared with Berzinsh et al’s experimental and many-body calculations results [27] in section 5.

2. Electron affinity and ISs

2.1. The experimental electron affinity as a guideline

As in our previous work on the IS in the sulfur electron affinity [30], the experimental electron affinity

\[ \Delta A_{\text{exp}} = E(\text{Cl}_2^3s^23p^5\ 2P^0_{3/2}) - E(\text{Cl}^-\ 3s^23p^6\ ^1S_0) \]  

(1)

is used as a precious guideline to set efficient pathways in the variational configuration spaces. Both 35Cl and 37Cl isotopes have a nuclear spin I = 3/2. For both isotopes, the ground state of the neutral chlorine is therefore split into four hyperfine structure levels \( F = 0, 1, 2, 3 \), where the \( F = 0 \) level has the lowest energy, while the ground state of the negative ion does not show a hyperfine structure since \( J = 0 \). The electron affinity measured by Berzinsh et al. [27],

\[ \Delta A_{\text{exp}} = 29.138.59(22) \text{ cm}^{-1} = 3.612.724(27) \text{ eV}, \]

is defined from the threshold energy and thus strictly corresponds to the difference between the lowest hyperfine level of the ground state of the neutral and the ground state of the anion. Compared to equation (1), this represents a difference of only 700 and 586 MHz for 35Cl and 37Cl, respectively, and is one order of magnitude smaller than the uncertainty of the measured electron affinity. In this work, we adopt a non-relativistic variational approach for targeting electron correlation (see section 3), and we need to estimate the average experimental electron affinity that would be measured if not resolving the fine-structure thresholds due to the J-splitting of the chlorine ground term \( \text{Cl}_2^3s^23p^5\ 2P^0_{1/2–3/2} \).

This average electron affinity can be expressed as

\[ \Delta A_{\text{exp}}^{\text{AV}} = \frac{6}{E_{1/2} - E_{3/2}}. \]

Using the NIST fine structure energy separation \( E_{1/2} - E_{3/2} = 982.3515 \text{ cm}^{-1} \), one finds \( \Delta A_{\text{exp}}^{\text{AV}} = 29.432.70(22) \text{ cm}^{-1} = 3.649.189 \text{ eV}, \) from which one subtracts the non-fine structure contribution \( \Delta E_{\text{NF}} = -0.015 \text{ eV} \) reported by de Oliveira et al. [2] to estimate the reference non-relativistic electron affinity

\[ \Delta A_{\text{ref}}^{\text{NR}} = \Delta A_{\text{exp}}^{\text{AV}} - \Delta E_{\text{NF}} = 3.664.24 \text{ eV} = 0.134.660 \text{ eV}. \]  

(3)

Adopting the \( (A' > A) \) convention where \( A \) is the mass number, the IS on the \( \Delta A \) is defined as

\[ IS(A', A) = \delta A \equiv \Delta A(A') - \Delta A(A). \]  

(4)

It can be expressed as the sum of the MS and FS contributions

\[ \delta A = \delta A_{\text{MS}} + \delta A_{\text{FS}}. \]  

(5)

Footnote 3 From the National Institute of Standards and Technology (NIST) critically evaluated data on atomic energy levels (http://physics.nist.gov/PhysRefData/ASD/levels_form.html).
2.2. Isotope mass shift

The MS of an atomic energy level is the energy displacement due to the inclusion of the dynamics of the nucleus in the Hamiltonian. The proper non-relativistic quantum mechanics treatment of the separation of the centre of mass motion and the motion of the $N$ electrons relative to the nucleus can be found in Johnson [31] and Bransden and Joachain [32]. The first (one-body) effect of the finite nuclear mass is to scale the infinite mass energies by the ratio $\mu/m_e = M/(M + m_e)$. The shift of the energy from the infinite-mass value defines the normal mass shift (NMS):

$$
\delta E_{\text{NMS}} = E_M - E_{\infty} = -\frac{m_e}{M + m_e}E_{\infty} = -\frac{\mu}{M}E_{\infty} = -\frac{m_e}{M}E_M.
$$

(6)

A second (two-body) correction to the energy, referred to as the SMS, is given by

$$
\delta E_{\text{SMS}} = \frac{M}{2(M + m_e)} \sum_{i<j} \mathbf{p}_i \cdot \mathbf{p}_j = \frac{\mu}{2(M + m_e)} \sum_{i<j} \mathbf{p}_i \cdot \mathbf{p}_j.
$$

(7)

Combining (6) and (7) for estimating the level mass isotopic shift ($\delta E_{\text{MS}} = \delta E_{\text{NMS}} + \delta E_{\text{SMS}}$), it is easy to obtain the expression of the mass contribution to the IS on the electron affinity (4)

$$
\delta \delta A_{\text{MS}} = \delta \delta A_{\text{NMS}} + \delta \delta A_{\text{SMS}}
$$

where $\delta A_{\text{SMS}}$ is the difference

$$
\Delta S_{\text{SMS}} = S_{\text{SMS}}(X) - S_{\text{SMS}}(X^-)
$$

of the expectation values defining the SMS parameters

$$
S_{\text{SMS}} = -\left\langle \Psi_\infty \sum_{i<j} \nabla_i \cdot \nabla_j \left| \Psi_\infty \right\rangle,
$$

(10)

calculated for the ground states of the neutral atom $X$ and the negative ion $X^-$. Note that (8) can be shown to be strictly equivalent to

$$
\delta \delta A_{\text{MS}} = \left( \frac{\mu}{M} - \frac{\mu'}{M'} \right) \left( \delta A_{\infty} - \frac{\hbar^2}{m_e} \Delta S_{\text{SMS}} \right)
$$

$$
+ \left[ \left( \frac{\mu}{M} \right)^2 - \left( \frac{\mu'}{M'} \right)^2 \right] \frac{\hbar^2}{m_e} \Delta S_{\text{SMS}},
$$

(11)

where the first term alone corresponds to the prescription of King [7].

The expectation value (10) is dominated by its Hartree–Fock value, i.e. in Cl, by the $(s, p)$ Vinti integrals [34] which contribute negatively. The differential SMS (9) between the neutral atom and the negative ion is itself dominated by the Vinti integrals involving the additional 3p electron in Cl$^-$. The mass polarization difference $\Delta S_{\text{SMS}}$ is therefore positive. The first term appearing in the MS on the electron affinity (11) makes the antagonism between the two positive contributions explicit, i.e. the electron affinity $\delta A_{\infty}$ by itself and the SMS parameter variation $(\hbar^2/m_e) \Delta S_{\text{SMS}}$, from which a strong cancellation between the electronic part of the NMS and SMS can be expected: classically, electrons tend to move in opposite directions, as beautifully illustrated by Krause et al [4] in the two-electron case, and the nucleus tends to be slower than expected from the one-electron contributions. The SMS term is usually the bottleneck in the calculation of the IS of light systems and most of our effort is aimed at a robust estimation of this effect in the non-relativistic level of approximation.

The nuclear masses have been estimated by subtracting the total electron mass from the atomic masses of $^{35}\text{Cl}$ and $^{37}\text{Cl}$ taken from [35], i.e. $M(^{35}\text{Cl}) = 34.95952682(4)\text{ u}$ and $M(^{37}\text{Cl}) = 36.95657673(5)\text{ u}$.

2.3. Isotope field shift

According to [36, 37], the FS on the electron affinity can be estimated from the following expression:

$$
\delta \delta \Delta \Phi_{\text{FS}} = 4\pi \left[ \rho(0)^X_{\text{NR}} - \rho(0)^{X^-}_{\text{NR}} \right] \frac{\hbar^2}{4\pi M} f(Z)^{A'} [(\langle r^2 \rangle)_{\text{X}} - (\langle r^2 \rangle)_{\text{X}^-}],
$$

(12)

where $\rho_{\text{NR}}(0)$ is the spinless total electron density [38] at the origin, and where $f(Z)$ corrects for the fact that we use the non-relativistic electronic density for a point nucleus. Its value $f(Z = 17)^{35,37} = 16.940\text{ mK fm}^{-2} = 507.8\text{ MHz fm}^{-2}$ is taken from the compilation of Auftmuth et al [39].

The knowledge of the nuclear charge distributions of chlorine isotopes is unfortunately limited [10]. The root mean square (rms) nuclear charge radii $(\langle r^2 \rangle)^{1/2}$ resulting from elastic electron scattering measurements have been reported by Briscoe et al [40] for both isotopes:

$$
(\langle r^2 \rangle)^{35}_{\text{Cl}} = 3.384(15)\text{ fm},
$$

$$
(\langle r^2 \rangle)^{37}_{\text{Cl}} = 3.388(15)\text{ fm},
$$

on the basis of phase-shift fits to a three-parameter Fermi distribution. For $^{35}\text{Cl}$, the latter value strongly disagrees with the $(\langle r^2 \rangle)^{35}_{\text{Cl}} = 3.335(18)\text{ fm}$ rms value extracted from earlier muonic x-ray measurements [41]. To evaluate the difference $\delta (\langle r^2 \rangle)^{35,37} = (\langle r^2 \rangle)^{37} - (\langle r^2 \rangle)^{35}$ appearing in (12), we choose for consistency, the two above values recommended by Briscoe et al [40] and also adopted in De Vries et al’s compilation [42], i.e.

$$
\delta (\langle r^2 \rangle)^{35,37} = -0.03(24)\text{ fm}^2.
$$

(13)

Note that Berzinh et al used for their FS estimation [27] the value of $\delta (\langle r^2 \rangle)^{35,37} = +0.12(12)\text{ fm}^2$ that can also be derived from Briscoe et al’s charge distribution parameters, but obtained using two-parameter Fermi models. This positive value is in line with the result $\delta (\langle r^2 \rangle)^{35,37} = +0.127\text{ fm}^2$ that can be calculated from the rms of Angeli’s compilation [43] that
has been determined by averaging the charge radii extracted from different sources [44]. In view of the large dispersion of nuclear data, we think that it is preferable to use the same reference for both isotopes to maintain some coherence.

3. Computational strategy

3.1. MCHF calculations

We use MCHF wavefunctions built on orthonormal numerical radial orbitals using the atsp2k package [45]. Such an expansion is written as

\[ \Psi_{\text{MCHF}}(\gamma LS) = \sum_i c_i \Phi_i(\gamma LS), \]

where the configuration state functions (CSFs) \( \Phi_i(\gamma LS) \) are symmetry-adapted linear combinations of Slater determinants. In the MCHF theory, both one-electron numerical radial functions \( P_n(r) \) and the interaction coefficients \( c_i \) are optimized [46, 47]. The resolution of the secular equations associated with the Hamiltonian matrix built with the current one-electron orbital basis is usually referred to as the CI step of the MCHF procedure [48]. The CSF basis is often further extended to capture higher order excitations and to get a better description of the desired eigenvector, using the frozen set of MCHF one-electron orbitals. Although the MCHF wavefunction (14) can be classified as belonging to the general CI wavefunction family [49], we will restrict in this work the use of CI calculations to those based on the Hamiltonian diagonalization in a pre-optimized orbital set (see section 3.4).

3.2. Construction of the CSF spaces

We use a similar approach and notation as in [30]. First, a multireference (MR) configuration set is selected. Then, the active space is set to maintain some coherence. For CI, we adopt two different approaches, leading to significantly different \( P_n(r) \) sets. Firstly, we select only the most important configurations in the MR set, omitting the single excitations conserving \( l \):

\[ \text{MR}_{14} = \{ \text{Ne}\}[3s^23p^6, 3s^23p^33d^2, 3s^23p^34p^2, 3s^13p^53d^1], \]

\[ \text{MR}_{15} = \text{MR}_{14} \cup \{ 3s^13p^43d^14f^1 \}. \]

Secondly, we use a systematic approach based on the following MR space:

\[ \text{MR}_2 = [\text{Ne}][3s, 3p][3^1][3, 4]^1. \]

MCHF calculations are performed for various \( n_{\text{max}} \), ranging from 4f to 11k, the core orbitals being either optimized (MCHF) or fixed to their HF shape (FC-MCHF). Table 1 presents the configuration weights obtained in the FC-MCHF calculations. These weights are defined as the summed contribution of all CSFs \( \Phi_i \) belonging to a given configuration:

\[ w = \sqrt{\sum_{\Phi_i \in \text{config}} c_i^2}. \]

Contrary to the MR_{14}(CI), MR_{15}(CI) and MRD(Cl^{-}) lists, the use of MR2(CI) and MRT(Cl^{-}) reference lists favours the apparition of large weights for the single substitutions \( 3s \rightarrow 4s \) and \( 3p \rightarrow 4p \) by a mechanism identified by the authors [50]. Very similar wavefunctions can be constructed with and without the predominance of the \( nl \rightarrow nl' \) single excitations, the limit case occurring when the wavefunction is invariant under the rotations between the orbitals of a given \( l \). This flexibility of the MCHF optimization minimizes the error made by truncating the full expansion of the wavefunction but comes with the price of relatively ‘dilute’ eigenvectors and a slower numerical convergence. Other manifestations of this effect can be found in [30].

3.4. Core-valence CSF spaces

It has been shown by the authors that orbitals optimized through valence-correlation calculations can also be used to efficiently describe core-correlation effects [51]. We therefore use the MCHF orbitals optimized on the valence CSF expansions, as described in section 3.1, to investigate the effects of opening the [Ne]-core. Following the hierarchy of table 1, subsets of \( p \) configurations are selected. For each \( p \), all the single and double subshell substitutions of the corresponding MR in [11k] are generated, allowing at the most one hole in the \( n = 2 \) shell and none in 1s. These lists are finally reduced with respect to the full MR according to the building rule (15). The \( p \) values selected for each MR (16–19) are presented in table 2.
Table 1. Weights of the configurations composing the MR14, MR15, and MR2 sets of Cl and the MRD and MRT sets of Cl\(^-\) in the corresponding MR-I[11k] wavefunctions with the core orbitals fixed at the HF approximation. \(\#\) is the index of each configuration.

| Configuration       | MR14  | MR2  | \# |
|---------------------|-------|------|----|
| \(3s^23p^6\)        | 0.9569| 0.9374| 1 |
| \(3s^23p^33d^2\)    | 0.1903| 0.1835| 2 |
| \(3s^23p^33d^1\)    | 0.1143| 0.1792| 3 |
| \(3s^23p^34p^2\)    | 0.0831| 0.1098| 4 |
| \(3s^43p^4\)        | 0.0910|       | 5 |
| \(3s^63p^34d^1\)    | 0.0690|       | 6 |
| \(3s^63p^24d^2\)    | 0.0629|       | 7 |
| \(3s^63p^44f^2\)    | 0.0126|       | 8 |
| \(3s^63p^6\)        | 0.0048|       | 9 |

MR15 configuration weights:

| Configuration       | MR15  |       |     |
|---------------------|-------|------|-----|
| \(3s^23p^33d^2\)    | 0.9652|       |     |
| \(3s^23p^33d^1\)    | 0.1900|       |     |
| \(3s^23p^34p^2\)    | 0.1140|       |     |
| \(3s^23p^34p^1\)    | 0.0831|       |     |
| \(3s^23p^34p\)      | 0.0704|       |     |

MRD configuration weights:

| Configuration       | MRD  | MRRT |     |
|---------------------|------|------|-----|
| \(3s^23p^6\)        | 0.9469| 0.9124| 1  |
| \(3s^23p^43d^2\)    | 0.2090| 0.2592| 2  |
| \(3s^23p^44p^2\)    | 0.1283| 0.2066| 3  |
| \(3s^23p^44p\)      | 0.0737| 0.0876| 4  |
| \(3s^23p^43d\)      | 0.0711| 0.0849| 5  |
| \(3s^23p^44d\)      | 0.0639| 0.0769| 6  |
| \(3s^23p^44d^1\)    | 0.0528| 0.0738| 7  |
| \(3s^23p^44d^2\)    | 0.0517| 0.0539| 8  |
| \(3s^23p^44d^3\)    | 0.0455| 0.0535| 9  |
| \(3s^23p^45d\)      | 0.0399| 0.0448| 10 |
| \(3s^23p^45d^1\)    | 0.0364| 0.0441| 11 |
| \(3s^23p^45d^2\)    | 0.0355| 0.0413| 12 |
| \(3s^23p^45d^3\)    | 0.0292| 0.0375| 13 |
| \(3p^23d\)          | 0.0272| 0.0348| 14 |
| \(3p^23d^2\)        | 0.0261| 0.0298| 15 |
| \(3p^23d^3\)        | 0.0232| 0.0291| 16 |
| \(3p^24p\)          | 0.0207| 0.0256| 17 |
| \(3p^24p^2\)        | 0.0203| 0.0252| 18 |
| \(3p^24p^3\)        | 0.0190| 0.0234| 19 |
| \(3p^24s\)          | 0.0178| 0.0232| 20 |
| \(3p^24d\)          | 0.0140| 0.0209| 21 |
| \(3p^24f\)          | 0.0126| 0.0182| 22 |
| \(3s^13p^44s\)      | 0.0046| 0.0138| 23 |

Table 2. Values of \(p\) chosen to perform the corresponding open-core CI calculations for each MR of Cl and Cl\(^-\).

| Acronym/notation | Description | Section |
|------------------|-------------|---------|
| CI               | Configuration interaction | 3.1/3.4 |
| CSF              | Configuration state function | 3.1 |
| FC               | Frozen core | 3.3 |
| FS               | Field shift | 2.1 |
| IS               | Isotope shift | 2.1 |
| MCHF             | Multiconfiguration Hartree–Fock | 3.1 |
| MR               | Multireference | 3.2 |
| MRD, MRT         | MR used for MCHF on Cl\(^-\) | 3.3 |
| MR\(_p\)         | MR for open-core CI | 3.4 |
| MR\(_14\), MR\(_{15}\), MR\(_2\) | MR used for MCHF on Cl | 3.3 |
| MR\(_{14}\)       | MR used for Cl | 4.2 |
| MR-I             | MR-interacting CSF space | 3.2 |
| MS               | Mass shift | 2.1 |
| NMS              | Normal mass shift | 2.2 |
| SMS              | Specific mass shift | 2.2 |
| \([n_{max}/n_{max}]\) | orbital active set | 3.2 |
| \((r, p)\)       | Open-core CI CSFs spaces | 4.2 |

4. Results and discussion

In order to help the reader, table 3 summarizes the acronyms and notations used in this section.

4.1. Valence results

The results of the MCHF and FC-MCHF calculations using the multireferences MRD for Cl\(^-\) and MR2 for Cl, with \(n_{max}=9k\), \(10k\), and \(11k\) are presented in table 4. The A\(^\Delta\) and \(\Delta\_{SMS}\) values converge smoothly with the number of correlation layers but a significant difference is found between the MCHF and FC-MCHF approaches. The ground state of Cl\(^-\) is more stabilized by the optimization of the core orbitals than the one of Cl. The impact on the difference of mass polarization parameters is enormous (\(\approx 36\%\)), leading to a variation of the IS of about 70%. The MCHF results of table 4 are in agreement with the value of the differential mass polarization \(\Delta\_{SMS}=0.091(25)\) \(a_{25}^\Delta\) extracted from the experiment [27] and the \(\Delta_{Nef}\) value (3). It should however be noted that, due to the total wavefunction symmetry properties, the core optimization in the MCHF calculations leads to significantly different contributions in Cl\(^-\) and Cl. Indeed, a large rotation of the \(P_{22}(r)\) and \(P_{20}(r)\) radial functions is allowed in Cl\(^-\) as it leaves the dominant contribution to the wavefunction \((1s^22s^22p^6)^2s^23p^6\) invariant. Contrary to the anion, this effect is suppressed in the neutral atom by the large energy gap between \(2p^63p^6\) and \(2p^33p^6\). Figure 1 illustrates the dramatic mixing of the core and valence occurring in Cl\(^-\) as compared to Cl. The plot at the top shows the total radial density...
Table 4. Total energies ($E$, in $E_h$), $S_{\text{SMS}}$ parameters (in $a_0^{-2}$) and the size of the expansions (NCSF) in the MRD-I model of Cl$^-$ and in the MR2-I model of Cl for the largest active sets. The core-orbitals are either fixed to their HF shapes (FC-MCHF) or optimized (MCHF). The electron affinity ($^\dagger A$) and $\Delta S_{\text{SMS}}$ calculated using these models are reported in the third part of the table.

| $nl$ max | NCSF | $E$ | $S_{\text{SMS}}$ | $E$ | $S_{\text{SMS}}$ |
|----------|------|-----|------------------|-----|-----------------|
| Cl$^-$ (MRD) | 9k | 113 691 | $-459.838 5962$ | $-80.445 6256$ | $-459.839 4636$ | $-80.420 4925$ |
|          | 10k | 159 948 | $-459.838 8245$ | $-80.445 8813$ | $-459.839 6907$ | $-80.420 8569$ |
|          | 11k | 214 416 | $-459.838 9311$ | $-80.446 0807$ | $-459.839 7916$ | $-80.421 0037$ |
| Cl(MR2) | 9k | 291 878 | $-459.704 5818$ | $-80.324 8911$ | $-459.704 9422$ | $-80.331 9936$ |
|          | 10k | 410 462 | $-459.704 7414$ | $-80.325 1537$ | $-459.705 0994$ | $-80.332 2030$ |
|          | 11k | 550 117 | $-459.704 8192$ | $-80.325 3422$ | $-459.705 1767$ | $-80.332 3553$ |

| $nl$ max | $^\dagger A$ | $\Delta S_{\text{SMS}}$ | $^\dagger A$ | $\Delta S_{\text{SMS}}$ |
|----------|---------------|----------------|---------------|----------------|
| 9k       | 0.134 0144    | 0.120 7345     | 0.134 5215    | 0.088 4989     |
| 10k      | 0.134 0831    | 0.120 7276     | 0.134 5913    | 0.088 6538     |
| 11k      | 0.134 1119    | 0.120 7384     | 0.134 6149    | 0.088 6483     |
| Exp      | 0.134 7(1)$^a$ | 0.091(25)      | 0.134 7(1)$^a$ | 0.091(25)      |

$^a$ $S_{\text{SMS}}$ (see equation (3)).

Table 5. Total energies ($E$, in $E_h$), $S_{\text{SMS}}$ parameters (in $a_0^{-2}$) and the size of the expansions (NCSF) in the MRT-I model for Cl$^-$, in the MR1$_{4}$-I and MR1$_{5}$ models for Cl. The active set is limited to 9k, 10k and 11k and the core orbitals are fixed to their HF shapes.

| $nl$ max | NCSF | $E$ | $S_{\text{SMS}}$ |
|----------|------|-----|------------------|
| Cl$^-$ (MRT) | 9k | 330 083 | $-459.839 5099$ | $-80.432 1726$ |
|          | 10k | 467 617 | $-459.839 7392$ | $-80.432 4083$ |
|          | 11k | 630 131 | $-459.839 8463$ | $-80.432 6017$ |
| Cl(MR1$_{4}$) | 9k | 65 286 | $-459.703 5158$ | $-80.324 7147$ |
|          | 10k | 91 915 | $-459.703 6706$ | $-80.324 9490$ |
|          | 11k | 123 357 | $-459.703 7494$ | $-80.325 1612$ |
| Cl(MR1$_{5}$) | 9k | 152 483 | $-459.704 4618$ | $-80.323 3889$ |
|          | 10k | 212 132 | $-459.704 6178$ | $-80.323 6181$ |
|          | 11k | 282 047 | $-459.704 6972$ | $-80.323 8321$ |

calculated with the program DENSITY [38] from the Cl$^-$ MCHF wavefunction. In a closed-core calculation, this total density can easily be separated into its [Ne]-core contribution and its valence contribution. It is compared to the valence radial density of neutral chlorine. In the bottom panel of figure 1, we present the total difference of radial density between Cl$^-$ and Cl as well as its core and valence contributions. It is usually accepted that the core could change only slightly when comparing the neutral atom with its negative ion [1]. This is indeed observed in the total radial density difference, the ‘extra’ electron of Cl$^-$ being efficiently screened out of the [Ne]-core. However, we can also observe that it is the result of a large compensation between the core and valence contributions. It reveals that ‘relaxing the core’ does not mean the same thing in Cl and Cl$^-$.

Therefore, the MCHF orbitals cannot be used in the open-core Cl calculations.

Table 5 presents the FC-MCHF calculations MR1$_{4}$-I and MR1$_{5}$-I of Cl and MRT of Cl$^-$ for [9k], [10k] and [11k]. Note that from the comparison of tables 4 and 5, the energy values of the MR1$_{5}$-I and MR2-I models are in close agreement but the corresponding $S_{\text{SMS}}$ parameters do not compare so well, the mass polarization expectation values of the MR2 based approach being in better agreement with the MR1$_{4}$-I model. It should also be observed that the MR2-I CSF spaces are almost twice as large as those of MR1$_{5}$-I for a given number of correlation layers.

4.2. Open-core CI analysis and error estimation

In the following, we denote the Cl and Cl$^-$ models ($r$, $r'$) and ($r''$, $r'''$) respectively, $r/r'$ denoting the used MR, i.e. either 1$\alpha$, 1$\beta$, 2 for Cl or 1$\alpha$, 1$\beta$, 1$\gamma$ for Cl$^-$. The full array of the results of the open-core CI calculations on Cl and Cl$^-$ are reported in table 6. To extract the differential $\Delta S_{\text{SMS}}$ value from our results, we need some guideline. In valence calculations, this guideline is the number of correlation layers. Unfortunately, in the open-core CI approach, there is no satisfactory intrinsic convergence path in the space of the calculation parameters $r$, $r'$, $p$ and $p'$. However, thanks to the correlation observed between the energy and the mass polarization expectation value [30, 52], we are able to use the reference $S_{\text{SMS}}$ estimated in section 2.1 as a guideline.

Figure 2 plots the $S_{\text{SMS}}$ results obtained in the ($r$, $p$) model ($S_{\text{SMS}}(r, p)$) versus the energies $E(r, p)$, for Cl and Cl$^-$ in plots (a) and (b) respectively. The $p$-values are given in table 2. Note that the same scale is used in both the plots. The $p = 1$ points are outside the frames. In order to extend the results of the MR1$_{5}$ model, we add the configuration 3$s^3$p$^{4}$s$^{4}$p$^{4}$ to MR1$_{5}$, generate the corresponding (1$\alpha$, 6) open-core CSF list and perform a CI calculation on this space using the MR1$_{5}$-I[11k] orbital set. In the case of Cl$^-$, the convergence in $p$ (from right to left in figure 2(a)) is remarkably clean, with good consistency between the results obtained with the two MR. Even though the correlation between $E(r, p)$ and $S_{\text{SMS}}(r, p)$ of CI calculations is apparent in figure 2(b), it is less precise.

Fitting the eight last points based on the MRT model of Cl$^-$ (see tables 6), we obtain (in atomic units)

$$S_{\text{SMS}}(\text{Cl}^-) = -16.6(7) [E(\text{Cl}^-) - \bar{E}] = 79.8538(2),$$

where $\bar{E} = -459.904 085 \ E_h$ is the average of the energies of the fitted points. If all the aligned points of figure 2(a) are fitted, i.e. if the five last points for MRD are also included in the fit, the
angular coefficient becomes \(-17.5(4)\). It gives an indication of the uncertainty of the fit considering the convergence with respect to the used MR \((r')\). The relation (21) is illustrated by a plain line in figure 2(a), the dashed lines being the lower and upper limits for a 1.3 uncertainty on the angular coefficient and a \(2.10^{-4} \alpha_0^{-2}\) uncertainty on the offset. With these upgraded uncertainties, estimating the Cl\(^-\) total energy from the \textit{ab initio} neutral atom value and the reference non-relativistic electron affinity (see equation (3)),

\[
E (\text{Cl}^-) = E (\text{Cl}) - \varepsilon_{\text{A}^\text{NR}} \, \text{ref},
\]

(22)
and inserting (21) in (9), we obtain
\[ \Delta S_{\text{SMS}} = S_{\text{SMS}}(\text{Cl}^-) + 16.6(1.3) \left[ E(\text{Cl}^-) - \langle A^\text{NR}_\text{ref} \rangle - E \right] + 79.8538(2), \] (23)
from which the corresponding \( S_{\text{SMS}}(\text{Cl}^-) = S_{\text{SMS}}(\text{Cl}) - \Delta S_{\text{SMS}} \) value can be calculated. For each \((r,p)\) open-core CI calculation performed on Cl (see table 6), table 7 gives the Cl\(^-\) energies and \( S_{\text{SMS}} \) and the corresponding \( \Delta S_{\text{SMS}} \) values calculated from equations (22) and (23). We regroup the results of the models with \( r = 1_4, 1_5 \) and \( 1_6 \) and order them by decreasing energy. Note that the energies reported in this table never go below the \(-459.9052 \text{ E}_\text{h}\) limit estimated by extrapolating the values of table 6. The quoted errors only take into account the uncertainty deduced from the CI\(^-\) calculations convergence and from the estimated uncertainty on \( \langle A^\text{NR}_\text{ref} \rangle \). All the calculations agree with the experiment \( \Delta S_{\text{SMS}} = 0.091(25)a_0^{-2} \). From table 7, we adopt the value \( 0.096(3)a_0^{-2} \). Using the fact that the results of \((r,p) = (2, 15)\) and \((1_5, 6)\) models are consistent, we estimate the uncertainty associated with the convergence of the calculations on Cl by taking the difference between the \( (2, 12) \) and \((1_5, 5)\) values, leading to the final estimation \( \Delta S_{\text{SMS}} = 0.096(9)a_0^{-2} \).

5. Comparison with experiment and conclusion

In section 3.3, we elaborate large-scale valence MCHF models and subsequently add open-core CSFs expansions. Focusing on the differential effects, more flexibility is added in the Cl\(^-\) models than in the ones of Cl. The correlation between the energy and the mass polarization expectation value in a sequence of calculations, already observed in earlier work [52], allows one to do a linear regression around the results of the largest Cl\(^-\) calculations (see section 4.2). Guided by the experimental non-relativistic electron affinity estimated in section 2.1, we adjust the Cl\(^-\) SMS parameters from the resulting simple law linking the \( \Delta S_{\text{SMS}} \) value with the neutral chlorine energy and the SMS parameter. A robust uncertainty for the (valence+core–valence) correlation contributions to the IS is deduced. However, core–core correlation effects are known to be important in IS calculations [53, 54] and should be included in more accurate approaches as well as relativistic corrections.

Table 8 compares the results of our work with the experimental and theoretical values of Berzinsh et al [27]. The experimental NMS of 741 MHz is used to deduce the total IS so that a cleaner theory/experiment comparison is found in the residual IS (RIS = IS – NMS). The uncorrelated fully relativistic Dirac–Fock (DF) results from Berzinsh et al [27] are also reported. For each model, we give the SMS, total MS (MS = NMS + SMS) and FS. As pointed out by Berzinsh et al [27], their estimated field isotope shift of

![Figure 2](image-url)
the electron affinity is well below the error bars of the IS measurement. The difference between their FS values and ours is caused by another choice of $\delta(r^2)$ change between isotopes (see discussion in section 2.3). In this respect, the uncertainty associated with the very small FS constitutes a large source of uncertainty in the final theoretical RIS and IS values. The calculations of [27] include the relativistic effects but only the lowest order correlation corrections, predicting an RIS opposite to the measured one.

The results of the MRD-I[11k] for Cl$^-$ and MR2-I[11k] obtained in section 4.1 are combined to give the valence frozen core (FC-MCHF) and optimized core (MCHF) results presented in table 8. At first sight, relaxing the core orbitals lifts the discrepancy between the valence model and the experimental values. However, in this work, we observe that the optimization of the core orbitals of Cl and Cl$^-$ leads to significantly different contributions, a priori destroying the balance between the core/valeence distinction of the two systems. However, it is interesting to consider the possibility that this agreement is not accidental.

The IS on the electron affinity is found to be anomalous for beryllium [55] and oxygen [17, 29], corresponding to a smaller electron affinity for the heavier isotope. For sulfur, theory also predicts an anomalous IS, allowed by the large electron affinity that determines the (normal) IS. The normal–anomalous IS change corresponds to the crossing between the $(\hbar^2/m_e)\Delta_{SMS}$ and $\hbar\Delta_{SMS}$ positive values defined by equation (9). For sulfur (Z = 16) for which the sign of the IS on the electron affinity is not definitive [30].

As pointed out by Andersson et al [21], the analysis of the electron affinities of atoms shows that, with the exception of the hydrogen atom, calculated electron affinities are less accurately known than measured ones. However, we have shown in [30] that the theoretical IS values on the electron affinity could be more accurate than the observed ones. In this work, we demonstrated that theoretical calculations of the electronic factors of the mass contribution have evolved remarkably, solving a longstanding discrepancy between the calculated and measured SMS on the electron affinity of chlorine.

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Table 8. Experimental and theoretical ISs on the $A^-$ for the chlorine isotopes $A = 37, 35$. The experimental NMS of 0.741 GHz is used to obtain the IS. All values are in GHz. Valence MCHF and FC-MCHF are based on the models MRD and MR2 respectively for Cl$^-$ and Cl. The final value is deduced as explained in section 4.2.

|         | SMS | MS  | FS   | RIS   | IS   |
|---------|-----|-----|------|-------|------|
| HF      | −1.348 | −0.607 | −0.003(22) | −1.351(22) | −0.610(22) |
| val. FC−MCHF | −0.674 | +0.067 | −0.002(20) | −0.676(20) | +0.065(20) |
| val. MCHF | −0.495 | +0.246 | −0.002(21) | −0.497(21) | +0.244(21) |
| final results | −0.535(51) | +0.206(51) | −0.003(22) | −0.538(72) | +0.203(72) |

Berzinsh et al [27]
