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Isotope shift in the electron affinity of beryllium

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Abstract

The study of the isotope shift in the electron affinity is interesting for probing correlation effects. Experiments that allow this property to be measured are rare, being difficult to realize, while accurate calculations remain a challenge for atomic theory. The present work focuses on the theoretical estimation of the isotope shift in the electron affinity of Be (2s2p ^{3}P^o), using correlated electronic wavefunctions obtained from multiconfiguration Hartree–Fock and configuration interaction variational calculations. The reliability of the correlation models is assessed from a comparison between the observed and theoretical electron affinities, and between theoretical isotope shift values for the 2s2p ^{3}P^o–2s^2 ^{1}S transition of neutral beryllium. The sign and the magnitude of the difference between the mass polarization term expectation values obtained for the neutral atom and the negative ion are such that the resulting isotope shift in the electron affinity is 'anomalous', corresponding to a smaller electron affinity for the heavier isotope.

1. Introduction

Negative ions are atomic systems of growing interest owing to the continuous development of experimental techniques. The review paper by Anderson *et al* [1] reveals the enormous progress realized in this field since the previous survey articles [2, 3]. These spectacular experimental developments are still on their way, leading to the possibility of measuring electron affinities accurately [4], sometimes for different isotopes [5], or cross sections for the electron impact detachment [6]. It is well known that electron correlation plays a crucial role in the calculation of properties of negative ions [7]. A review of many-body effects in negative-ion photodetachment can be found in [8]. The comparison of theory and experiment through the isotope shift in the electron affinity is of particular interest for probing correlation effects that affect both properties. Experiments that allow this effect to be measured are difficult to realize while accurate calculations remain a challenge for atomic theory.

The electron affinities of atomic hydrogen and deuterium have been determined by Lykke *et al* [9] using tunable-laser threshold-photodetachment spectroscopy. The isotope shift in the electron affinity has been found to be 3.2 ± 0.7 cm^{-1}, confirming the predicted theoretical shift of 3.6 cm^{-1} calculated from the expectation values of Pekeris [10]. Drake [11] estimated this shift with a spectacular accuracy, 3.613 037 cm^{-1}, correct to the figures quoted, including the finite mass and recoil corrections to the relativistic and QED terms up to order α^3 Ryd, as well as the nuclear volume effect. The positive isotope shift corresponds to a larger electron affinity for deuterium than for hydrogen, the normal mass shift (NMS) effect being reinforced by the specific mass shift (SMS) correction.

The isotope shift in the electron affinity between ^{37}Cl and ^{35}Cl has been determined from tunable-laser photodetachment spectroscopy measurements by Berzinsh *et al* [12]. Observation also reveals a 'normal' isotope shift (i.e. an electron affinity larger for the heavier isotope) of 0.22(14) GHz, of which $-0.51(14)$ GHz is due to the specific mass shift. As shown by the pioneer many-body calculations presented in the same work [12], a theoretical estimation of the isotope-specific mass shift contribution in the electron affinity of such a large system, was considered beyond the (by then) possible state-of-the-art computational techniques. A conclusion made by these authors was that theory, predicting a specific mass shift of +0.50 GHz, having the correct order of magnitude but the wrong sign, could not lead to a quantitative description due to the omission of higher-order correlation effects. It was then suggested to attempt more precise experiments on other negative ions, with S$^-$ as a possible candidate, or to investigate 'few-electron' systems, such as Li$^-$, for which more accurate calculations could be performed. In this line, a new determination of the Li electron affinity has been reported by Haeffler *et al* [13] using a state selective photodetachment spectroscopic method but the measurements were unfortunately limited to the ^{7}Li isotope, shedding no light on the isotope shift in the electron affinity. A 'normal' isotope shift is however expected from the specific mass shift parameters evaluated by Froese Fischer [14] for Li and Li$^-$.

A satisfactory agreement between theory and observation was found for the isotope shift in the oxygen electron affinity. Valli *et al* [5] measured the electron affinities of ^{18}O and ^{16}O isotopes by using the photodetachment microscopy technique from which a negative isotope shift in the electron affinity of oxygen was found. This 'anomalous' character of the isotope shift, corresponding to a smaller electron affinity for the heavier isotope, was explained from the variational *ab initio* calculations by Godefroid and Froese Fischer [15] of the expectation value of the mass polarization term for both the neutral atom and the negative ion. The theoretical *ab initio* specific mass shift contribution to the electron affinity, was indeed found to be negative, and sensitively larger in absolute value than the (positive) normal mass shift contribution. This fact was confirmed through the measurements of the ^{17}O electron affinity by Blondel *et al* [16] owing to the high sensitivity of the photodetachment microscopy experiments that revealed electron images even for the rarest isotope ^{17}O$^-$ ion.

Another interesting testcase for a comparison of theory with observation could be the isotope shift in the electron affinity of beryllium. Atomic spectroscopy experiments on unstable beryllium isotopes indeed become possible owing to the ISOLDE facility at CERN [17]. Within this context, the feasibility of some experiments allowing the determination of the nuclear quadrupole moment of ^{7}Be from the observed hyperfine structure of the negative ion ^{7}Be$^-$ (2s2p^2 ^{4}P$_J$) has been investigated recently [18]. In the present work we report the first *ab initio* calculations of the isotope shift in the electron affinity of Be (2s2p ^{3}P^o) for various isotopic pairs involving the $^{11-7}$Be isotopes.

The necessary theoretical background for understanding the relevant parameters monitoring the isotope shift in the electron affinity is presented in section 2. The variational multiconfiguration Hartree–Fock (MCHF) method and the configuration interaction (CI) correlation models, based on the concept of the orbital and configuration-active spaces, are briefly described in section 3. The results are reported in section 4. In section 4.1, the theoretical evaluation of the electron affinity is studied, as a quality test of the wavefunctions describing both the neutral atom and the negative ion. In section 4.2, the reliability of the correlation models is further assessed, for the neutral atom, by a comparison of the theoretical isotope shift values for the 2s2p $^3\mathrm{P^o}$–$2\mathrm{s}^2\ ^1\mathrm{S}$ transition, evaluated with the present MCHF/CI wavefunctions, with the results of Chung and Zhu [19] using the full-core plus correlation (FCPC) method. In section 4.3, we study the corresponding convergence of the specific mass shift parameters allowing the estimation of the isotope shift in the electron affinity.

2. Theory

The isotope shift of an energy level arises from the addition of two effects, the mass shift and the field shift. The former accounts for the nuclear motion while the latter is due to changes in the nuclear charge distributions. The extended charge correction is known to be weak for light atoms [20] and is not considered in the present work.

The mass shift for the energy level of an N-electron atom with a finite nuclear mass can be derived by treating the mass polarization term

$$\frac{1}{M}\sum_{i<j}^{N}\mathbf{p}_i\cdot\mathbf{p}_j$$

as a small perturbation [21], where $\mathbf{p}_i$ is the momentum of the ith electron. Keeping only the first-order specific mass shift correction, the mass shift has the form [22–24]

$$E_M - E_\infty = -\frac{\mu}{M}E_\infty + \frac{\mu}{m_e}\frac{1}{M+m_e}\langle\Psi_\infty|\sum_{i<j}^{N}\mathbf{p}_i\cdot\mathbf{p}_j|\Psi_\infty\rangle \qquad (1)$$

where $\mu = m_e M/(m_e + M)$ is the reduced mass. E_∞ and Ψ_∞ are respectively the (negative) eigenvalue and eigenfunction of the infinite nuclear mass problem. The two terms of the right-hand side of this equation are known, respectively, as the normal mass shift and the specific mass shift. Expressing energy, masses and linear momentum in atomic units, equation (1) can be rewritten as

$$E_M = \frac{M}{1+M}E_\infty + \frac{M}{(1+M)^2}S_{\mathrm{SMS}} \qquad (2)$$

where

$$S_{\mathrm{SMS}} = -\langle\Psi_\infty|\sum_{i<j}^{N}\nabla_i\cdot\nabla_j|\Psi_\infty\rangle \qquad (3)$$

is often referred to as the specific mass shift parameter.

According to equation (2), the electron affinity of a given beryllium isotope, ^{M}Be, is given by

$$\begin{aligned}E_{\mathrm{a}}^{M} &= E_M(\mathrm{Be}) - E_M(\mathrm{Be}^-)\\ &= \frac{M}{1+M}E_{\mathrm{a}}^{\infty} + \frac{M}{(1+M)^2}\Delta S_{\mathrm{SMS}}\end{aligned} \qquad (4)$$

where E_{a}^{∞} is the beryllium electron affinity calculated with an infinite nuclear mass, and where

$$\Delta S_{\mathrm{SMS}} = S_{\mathrm{SMS}}(\mathrm{Be}) - S_{\mathrm{SMS}}(\mathrm{Be}^-).$$

The isotope shift in the electron affinity is the difference of the electron affinities between two different isotopes of masses M and M',

$$\begin{aligned}\Delta E_{\mathrm{a}}^{MM'} &= E_{\mathrm{a}}(^{M}\mathrm{Be}) - E_{\mathrm{a}}(^{M'}\mathrm{Be}) \\ &= \Delta E_{\mathrm{a}}^{\mathrm{NMS}}(^{M-M'}\mathrm{Be}) + \Delta E_{\mathrm{a}}^{\mathrm{SMS}}(^{M-M'}\mathrm{Be})\end{aligned} \tag{5}$$

with, according to (4),

$$\Delta E_{\mathrm{a}}^{\mathrm{NMS}}(^{M-M'}\mathrm{Be}) = \left[\frac{M}{1+M} - \frac{M'}{1+M'}\right] E_{\mathrm{a}}^{\infty} \tag{6}$$

and

$$\Delta E_{\mathrm{a}}^{\mathrm{SMS}}(^{M-M'}\mathrm{Be}) = \left[\frac{M}{(1+M)^2} - \frac{M'}{(1+M')^2}\right] \Delta S_{\mathrm{SMS}}. \tag{7}$$

Adopting the convention that the isotope M is heavier than the isotope M', $(M > M')$, the mass factor of (6) is always positive. Since E_{a}^{∞} of Be (2s2p $^3\mathrm{P}^{\mathrm{o}}$) is definitely positive, corresponding to a bound negative ion, the normal mass shift contribution $\Delta E_{\mathrm{a}}^{\mathrm{NMS}}$ to the isotope shift in the electron affinity is also positive. In contrast, the mass factor in equation (7) is always negative[3]. If $\Delta S_{\mathrm{SMS}} < 0$, the SMS and the NMS contributions will add up, giving rise to a normal isotope shift. In contrast, if this quantity is positive, the specific mass shift contribution to the isotope shift in the electron affinity counteracts the normal mass shift. In such a negative interference case, the specific mass shift contribution to the isotope shift on the electron affinity will depend on the balance between the NMS and SMS contributions. In some situations, the magnitude of the SMS effect can be large enough to produce an ‘anomalous’ isotope shift, i.e. a smaller electron affinity for the heavier isotope.

3. Computational strategy

The infinite nuclear mass eigenfunctions Ψ_∞ are calculated using the MCHF and CI methods. An MCHF wavefunction Ψ_∞ is expanded in terms of configuration state functions (CSF) $\{\Phi_i\}$ having the same $LSM_LM_S\pi$ symmetry but arising from different electronic configurations (γ_i),

$$\Psi(\gamma LSM_LM_S\pi) = \sum_{i=1} c_i \Phi(\gamma_i LSM_LM_S\pi). \tag{8}$$

The CSFs are built on the basis of one-electron spin–orbital functions

$$\phi_{nlm_lm_s} = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \varphi) \chi_{m_s}. \tag{9}$$

In the MCHF procedure both the sets of radial functions $\{P_{n_il_i}(r)\}$ and mixing coefficients $\{c_i\}$ are optimized to self-consistency by solving numerically and iteratively the multiconfiguration Hartree–Fock differential equations for the former and the configuration interaction problem for the latter [25].

The active space (AS) method [26, 27] is used for building the CSFs expansion (9). The core–core correlation effect being very important on the specific mass parameters [28] of Be states, we have used a full correlation model for generating the CSF. We considered for the first step, i.e. the MCHF optimization of the one-electron orbitals, all the simple (S) and double (D) excitations from the Hartree–Fock reference configuration to an increasing active

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[3] The mass factor of equation (7) can be rewritten as $(M - M')(1 - MM')/[(1 + M)(1 + M')]^2$ and is negative for any physical situation $(MM' \gg 1)$, with the convention $M > M'$ and remembering that the nuclear masses are expressed in atomic units.

Table 1. Total energies of Be (2s2p $^3P^o$) and Be$^-$ (2s2p^2 ^4P) together with the Be (2s2p $^3P^o$) electron affinity (E_a) for different SD-MCHF (first series) and SDTQ-CI (second series) configuration expansions. NCSF is the number of configuration state functions.

	Be (1s^{2}2s2p $^3P^o$)		Be$^-$ (1s^{2}2s2p^2 ^4P)		
Active set	E_{tot} (au)	NCSF	E_{tot} (au)	NCSF	E_a (eV)
HF	−14.511 5018	1	−14.509 0277	1	−0.0673
2	−14.511 5767	4	−14.509 0395	4	−0.0690
3	−14.553 3693	56	−14.552 7630	78	−0.0165
4	−14.559 7543	208	−14.566 1729	313	0.1746
5	−14.563 6590	502	−14.571 3284	784	0.2087
6g	−14.565 2854	942	−14.573 3203	1493	0.2186
7g	−14.565 8835	1528	−14.574 2324	2440	0.2272
8g	−14.566 1239	2260	−14.574 6172	3625	0.2311
9g	−14.566 2361	3138	−14.574 8012	5048	0.2331
10g	−14.566 2905	4162	−14.574 8912	6709	0.2340
SD[10g] ∪ TQ[3]	−14.566 5738	4230	−14.575 3383	6919	0.2385
SD[10g] ∪ TQ[4]	−14.566 6494	5238	−14.576 4941	110 62	0.2679
SD[10g] ∪ TQ[5]	−14.566 7212	7918	−14.576 8124	356 99	0.2746
SD[10g] ∪ TQ[6g]	−14.566 7304	105 98	−14.577 0444	859 76	0.2807
SD[10g] ∪ TQ[7g]	−14.566 7336	132 78	−14.577 2259	161 893	0.2855
SD[10g] ∪ TQ[8g]	−14.566 7347	159 58	−14.577 3036	263 450	0.2876
Other theory [31]					0.285(5)
Other theory [32]					0.2891(10)
Obs. [33]					0.290 99(10)

set of orbitals from $n = 2$ up to $n = 10$, with the angular momentum limitation $l_{max} = 4$ corresponding to g-orbitals for $n \geqslant 6$. The obtained active spaces are noted by 'n' for $n < 6$ and 'ng' for $n \geqslant 6$.

Once the radial functions have been determined, a configuration interaction calculation is performed over a set of configuration states. In the present work, the configuration lists used in the CI calculations have been produced by merging the configuration subspace created from single and double excitations to the '10g' active set (SD[10g]) with another subspace generated by allowing further triple and quadrupole excitations (TQ[x]) to smaller orbital active sets (x). This merging of CSF lists is denoted hereafter by the union '∪' symbol. The limited population constraint [29, 30] 'at least three electrons with $n \leqslant 4$' was adopted in this last step in order to keep the size of the multiconfiguration expansions manageable. The number of configuration state functions used in the MCHF/CI expansions (8) is denoted by NCSF.

4. Results

4.1. The Be electron affinity

In a recent paper [18], the relevant parameters for the calculation of the Be (2s2p $^3P^o$) electron affinity and the Be$^-$ (2s2p^2 $^4P_{1/2,3/2,5/2}$) hyperfine structure have been discussed. In the present approach we used the same largest set of one-electron orbitals optimized from the 10g-SD-MCHF expansions, but extended the CI configuration space considered by Nemouchi *et al* [18] by including the triple and quadrupole excitations up to the extra layer '8g'.

Table 1 shows the total energies of Be (2s2p $^3P^o$) and Be$^-$ (2s2p^2 ^4P), together with the electron affinity of Be (2s2p $^3P^o$) as a function of the SD-MCHF and SDTQ-CI expansions.

As can be seen from monitoring the electron affinity value with the CI configuration spaces, the convergence has not been achieved, even with the largest CI calculations. However, it has somewhat been improved relatively to [18] and it was worthwhile adding the extra layer in the CI space. The corresponding value of 0.2876 eV (with 263 450 CSF for the negative ion) is larger than the theoretical estimation of Olsen *et al* [31], but the convergence trend is in line with the larger theoretical value obtained by Hsu and Chung [32] and with the most recent experimental value [33] taking into account their quoted uncertainty. Table 1 undoubtedly reflects the high reliability of the used correlation models and the good quality of the wavefunctions that are used for estimating the isotope shift parameters discussed in section 4.3.

4.2. The isotope shift of the 2s2p $^3P^o$–2s^2 ^1S transition

The lack of experimental data and other theoretical results on the isotope shift in the electron affinity of beryllium does not allow us to make any comparison. However, in addition to the analysis of the electron affinity itself as a good accuracy indicator (see section 4.1), we are using the $^{10-9}$Be and $^{9-8}$Be isotope shift calculations as another test of reliability for the neutral system. Isotope shifts of the $1s^22snl$–$1s^22s^2$ transitions have been evaluated by Chung and Zhu [19] using the full-core plus correlation method. From the good agreement between this theory and experimental data [34] obtained for the 2s3d ^{1}D–2s^2 ^{1}S transition found in this work, one can infer the reliability of the FCPC results.

By using the MCHF and CI methods we have studied the convergence of the specific mass parameters for the states Be (2s^2 ^{1}S) and Be (2s2p ^{3}P^o) from which we deduced the $^{10-9}$Be and $^{9-8}$Be isotope shifts for the 2s2p ^{3}P^o–2s^2 ^{1}S transition, using the following formula:

$$
{}^{M-M'}\Delta\nu = \left\{ \left[\frac{M}{1+M} - \frac{M'}{1+M'} \right] [E(2s2p\ {}^3P^o) - E(2s^2\ {}^1S)] + \left[\frac{M}{(1+M)^2} - \frac{M'}{(1+M')^2} \right] [S_{SMS}(2s2p\ {}^3P^o) - S_{SMS}(2s^2\ {}^1S)] \right\} \times k.
$$

In this expression, atomic masses, energies and specific mass parameters are in atomic units and $k = 6579\,683.920\,735$ is the conversion factor calculated from the recommended values of the fundamental constants found on the NIST website [35] to get the frequency shift in GHz. The isotope masses have been taken from the compilation of Audi and Wapstra [36].

The results are given in table 2. Although the 10g-SD-MCHF results for the IS almost reproduce the one-configuration Hartree–Fock values, it should be realized from the comparison of the individual state contributions that this agreement is fortuitous, the electron correlation effects for both states being crucial. The triple and quadrupole excitations increase the transition isotope shift by 11%, arising from a larger effect on the ground state than on the excited state level isotope shift. The results obtained with the largest CI configuration space are in good agreement with the FCPC values calculated by Chung and Zhu [19]. This observation alone gives us confidence in our correlation models used for the four-electron system.

4.3. The isotope shift on the electron affinity

We give in table 3 the values of the specific mass parameters for Be$^-$ (2s2p^2 ^{4}P) and Be (2s2p ^{3}P^o) as well as the normal mass shift $\left(\Delta E_a^{NMS}\right)$, the specific mass shift $\left(\Delta E_a^{SMS}\right)$ and the isotope mass shift in the electron affinity (ΔE_a) for $^{11-9}$Be and $^{9-7}$Be. The isotope masses have been taken from the compilation of Audi and Wapstra [36].

Table 2. Specific mass shift parameters (in a_0^{-2}) for Be ($2s^2\ ^1S$), Be ($2s2p\ ^3P^o$) and $^{10-9}$Be and $^{9-8}$Be isotope shifts (in GHz) for the $2s2p\ ^3P^o$–$2s^2\ ^1S$ transition.

AS	S_{SMS} Be ($2s^2\ ^1S$)	S_{SMS} Be ($2s2p\ ^3P^o$)	Isotope shift transition $^{10-9}$Be	$^{9-8}$Be
HF	0.000 000 00	−0.210 127 92	10.8826	13.6882
2	0.006 882 43	−0.208 948 38	12.8641	16.1806
3	0.448 753 44	0.275 577 16	10.8561	13.6548
4	0.448 582 75	0.275 075 21	10.8808	13.6859
5	0.432 004 12	0.259 413 06	10.8112	13.5984
6g	0.430 686 66	0.257 242 18	10.8168	13.6054
7g	0.429 864 46	0.256 007 81	10.8308	13.6231
8g	0.429 512 10	0.255 624 34	10.8325	13.6252
9g	0.429 415 56	0.255 429 27	10.8360	13.6297
10g	0.429 347 39	0.255 329 26	10.8375	13.6315
SD[10g] ∪ TQ[3]	0.460 699 35	0.260 441 31	11.9946	15.0869
SD[10g] ∪ TQ[4]	0.461 811 78	0.261 024 27	12.0364	15.1394
SD[10g] ∪ TQ[5]	0.462 014 14	0.261 297 61	12.0361	15.1391
SD[10g] ∪ TQ[6g]	0.462 110 36	0.261 410 50	12.0392	15.1430
SD[10g] ∪ TQ[7g]	0.462 023 00	0.261 451 46	12.0347	15.1373
SD[10g] ∪ TQ[8g]	0.461 981 19	0.261 464 44	12.0326	15.1347
Other theory [14]			12.003	15.097

As we can see through table 3, the negative normal mass shifts found in the Hartree–Fock approximation and in the SD-MCHF correlation model up to the $n = 3$ active set, are coherent with the corresponding negative electron affinities given in table 1. The convergence of the normal mass shift indeed strictly follows, as it should (see equation (6)), the convergence trend of the electron affinity. Electron correlation has to be included beyond this active set for getting a correctly bound negative ion as observed, i.e. a positive electron affinity from which a positive normal mass shift is deduced.

The three HF rows of table 3 correspond, respectively, to the use of the Hartree–Fock method on the neutral atom (HF(Be)), on the negative ion (HF(Be^-)), and on the separately optimized states (HF) for the neutral atom and the negative ion. The sign of ΔS_{SMS} is positive in all the calculations that we have performed. It can be understood in the single-configuration Hartree–Fock approximation, adopting the same orbital basis set for describing both the negative ion and the neutral atom. We indeed know that the matrix elements of the mass polarization term (3) have the same angular part than the $k = 1$ exchange contributions to the electrostatic Coulomb interaction between the electrons [25]. The weight angular coefficients for the exchange integrals $G^1(nl, n'l')$ and the corresponding products of Vinti integrals $J(nl, n'l')J(n'l', nl)$ are then the same. Using this mapping, the specific mass shift parameters are given by

$$S_{SMS}(\mathrm{Be}) = -\tfrac{1}{3}[J^2(1s2p) + J^2(2s2p)]$$

and

$$S_{SMS}(\mathrm{Be}^-) = -\tfrac{2}{3}[J^2(1s2p) + J^2(2s2p)]$$

for, respectively, Be ($1s^22s2p\ ^3P^o$) and Be^- ($1s^22s2p^2\ ^4P$). The resulting difference, only valid in a *frozen* orbital model,

$$\Delta S_{SMS} = \tfrac{1}{3}[J^2(1s2p) + J^2(2s2p)]$$

Table 3. Specific mass shift parameters (in a_0^{-2}) for the negative ion and the neutral atom, normal mass shift (NMS), specific mass shifts (SMS) and isotope shifts (all in cm^{-1}) in the electron affinity E_a.

	Be$^-$ (2s2p^2 ^{4}P)	Be (2s2p ^{3}P^o)	$^{11-9}$Be isotope shifts (cm^{-1})			$^{9-7}$Be isotope shifts (cm^{-1})		
AS	S_{SMS}	S_{SMS}	ΔE_a^{NMS}	ΔE_a^{SMS}	ΔE_a	ΔE_a^{NMS}	ΔE_a^{SMS}	ΔE_a
HF(Be)	−0.420 255 84	−0.210 127 92	−0.006 028	−0.511 929	−0.517 957	−0.006 028	−0.798 454	−0.807 856
HF(Be$^-$)	−0.268 008 35	−0.134 004 18	−0.006 028	−0.326 471	−0.332 499	−0.006 028	−0.509 195	−0.518 597
HF	−0.268 008 35	−0.210 127 92	−0.006 028	−0.141 013	−0.147 041	−0.009 403	−0.219 937	−0.229 339
2	−0.267 792 71	−0.208 948 38	−0.006 028	−0.143 361	−0.149 543	−0.009 642	−0.223 599	−0.233 242
3	0.225 786 60	0.275 577 16	−0.001 477	−0.121 303	−0.122 781	−0.002 304	−0.189 196	−0.191 501
4	0.193 467 47	0.275 075 21	0.015 639	−0.198 819	−0.183 180	0.024 393	−0.310 097	−0.285 704
5	0.209 173 31	0.259 413 06	0.018 687	−0.122 398	−0.103 711	0.029 147	−0.190 903	−0.161 757
6g	0.202 451 93	0.257 242 18	0.019 577	−0.133 484	−0.113 907	0.030 536	−0.208 194	−0.177 659
7g	0.201 689 78	0.256 007 81	0.020 342	−0.132 334	−0.111 991	0.031 729	−0.206 400	−0.174 671
8g	0.201 089 38	0.255 624 34	0.020 694	−0.132 862	−0.112 168	0.032 278	−0.207 224	−0.174 947
9g	0.200 769 08	0.255 429 27	0.020 869	−0.133 167	−0.112 298	0.032 551	−0.207 700	−0.175 150
10g	0.200 588 58	0.255 329 26	0.020 956	−0.133 363	−0.112 407	0.032 686	−0.208 006	−0.175 320
SD[10g] ∪ TQ[3]	0.209 202 88	0.260 441 31	0.021 355	−0.124 831	−0.103 476	0.033 308	−0.194 698	−0.161 390
SD[10g] ∪ TQ[4]	0.218 435 24	0.261 024 27	0.023 987	−0.103 759	−0.079 772	0.037 414	−0.161 832	−0.124 418
SD[10g] ∪ TQ[5]	0.220 649 23	0.261 297 61	0.024 588	−0.099 031	−0.074 443	0.038 350	−0.154 458	−0.116 107
SD[10g] ∪ TQ[6g]	0.220 610 89	0.261 410 50	0.025 131	−0.099 399	−0.074 269	0.039 197	−0.155 032	−0.115 835
SD[10g] ∪ TQ[7g]	0.221 041 87	0.261 451 46	0.025 565	−0.098 449	−0.072 884	0.039 875	−0.153 550	−0.113 676
SD[10g] ∪ TQ[8g]	0.221 208 72	0.261 464 44	0.025 752	−0.098 074	−0.072 322	0.040 166	−0.152 966	−0.112 800

has to be positive, producing a negative SMS isotope shift on the electron affinity, as discussed in section 2.

The third row of table 3 illustrates the importance of the relaxation effects that have been captured by a separate optimization of the orbitals on the negative ion and the neutral atom. The SMS in the electron affinity is largely reduced by the relaxation and by the one-electron excitations implicitly contained in the Hartree–Fock approximation owing to Brillouin's theorem [37].

The largest '10g' orbital spaces obtained from the SD-MCHF correlation model look complete from the convergence achieved in the SMS parameters. The triple and quadrupole excitations included in the CI calculations affect considerably the specific mass shift operator mean value, more for the negative ion ($\simeq$10%) than for the neutral atom ($\simeq$2%). A satisfactory convergence, 10^{-3} and 10^{-4}, respectively, is achieved for the specific mass parameters of Be^- (2s2p ^{4}P) and Be (2s2p ^{3}P^o).

Columns 6 and 9 (ΔE_a for the two selected isotopic pairs) of table 3 reflect the importance of correlation effects on the isotope shift in the electron affinity. The SMS contribution to it $\left(\Delta E_a^{\mathrm{SMS}}\right)$ largely dominates the normal mass shift contribution $\left(\Delta E_a^{\mathrm{NMS}}\right)$. The analysis of the SMS parameters themselves, for either the negative ion or the neutral atom, illustrates the crucial role of single and double excitations considered in the MCHF expansions. As observed above, the role of triple and quadrupole excitations is not negligible, reaching 10% for the negative ion. While the large effects of single and double excitations on the SMS parameters are largely smoothed out when making their difference between the neutral atom and the negative ion, the effect of triple and quadrupole excitations is reinforced, reaching up to 30% on the ΔE_a value.

The specific mass isotope shift in the electron affinity $\left(\Delta E_a^{\mathrm{SMS}}\right)$ is found to be about four times larger, in absolute value, than the normal mass shift isotope $\left(\Delta E_a^{\mathrm{NMS}}\right)$. Counteracting the normal mass shift contribution, the isotope shift found in the electron affinity is definitely negative, corresponding to an 'anomalous' isotope shift.

5. Conclusion

We report large-scale MCHF and CI calculations of the isotope shift in the electron affinity of beryllium. The configuration expansions were generated with the systematic active space method by using a full correlation model. The calculated electron affinity is in good agreement with the recent experimental value. The 'anomalous' character of the isotope shift found in the present study, corresponding to a smaller electron affinity for the heavier isotope, is not specific to beryllium. It has already been observed in the case of the electron affinity of oxygen [15, 16], on the contrary of the chlorine case [12]. Before revisiting theoretically the difficult case of chlorine for which the many-body calculations failed to reproduce observation, it would be interesting to investigate, both theoretically and experimentally, the isotope shift on the electron affinity of lighter systems. We also hope that the present work, together with the theoretical work on hyperfine structures [18], will stimulate some new experiments on the negative beryllium ion for its various isotopes.

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