Isotope shift in the electron affinity of lithium

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Very accurate electron affinity (EA) calculations of ^{6}Li and ^{7}Li (and $^{\infty}$Li) have been performed using explicitly correlated Gaussian functions and a variational approach that explicitly includes the nuclear motion in the calculations (i.e., the approach that does not assume the Born–Oppenheimer approximation). The leading relativistic and quantum electrodynamics corrections to the electron affinities were also calculated. The results are the most accurate theoretical values obtained for the studied systems to date. Our best estimates of the ^{7}Li and ^{6}Li EAs are 4984.9842(30) and 4984.9015(30) cm^{-1}, respectively, and of the ^{7}Li/^{6}Li EA isotope shift is 0.0827 cm^{-1}.
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I. INTRODUCTION

Isotope shifts of measurable physical quantities are among the properties that are used to test the agreement between the experimental results and high-level theoretical calculations. Since these shifts depend on the nuclear masses of isotopes the calculations have to either be carried out without assuming the infinite-mass model (i.e., the Born–Oppenheimer approximation) or should include determination of finite-mass corrections with the use of the perturbation theory. In this work we employ the former approach. For atoms there are several isotope-sensitive quantities that can be very accurately measured with spectral methods and used for testing theoretical models used in the electronic structure atomic calculations. The atomic electron affinities are among those quantities.

In this work we determine the isotope shift effect in the electron affinity (EA) of lithium using high-accuracy theoretical calculations that involve all-electron explicitly correlated Gaussian functions. These types of functions have been used to calculate other three-, four-, and five-electron atomic systems.[1–3] The calculations also include the leading relativistic and quantum electrodynamics (QED) corrections. A brief review of the method used is given in Sec. II.

Even though there have been experiments concerning the EA of ^{7}Li,[4–8] there have been no reports on the measurement of the ^{6}Li electron affinity. The most accurate experimental ^{7}Li EA is likely the results of 4984.90(17) cm^{-1} reported by Haeffler *et al.*[8] However, the uncertainty of 0.17 cm^{-1} is still too high to allow distinction between the EAs of ^{6}Li and ^{7}Li. Thus, as the results of this work will show, the theoretical calculations are significantly more accurate in this case than the available experimental results. These calculations will hopefully challenge the experiment to remeasure the ^{7}Li EA more accurately and to find a way for performing a similar measurement for ^{6}Li.

The lithium EA has been a subject of numerous theoretical calculations. A comprehensive review of the earlier calculations performed in the framework of infinite-nuclear-mass (INM) approximation can be found in the work by King.[9] More recently two high accuracy calculations on the ^{7}Li EA were reported.[10,11] In the work by Pachucki and Komasa,[10] the INM variational calculations on ^{7}Li and ^{7}Li^{-} employing explicitly correlated Gaussians were performed first and the INM wave functions for these systems were subsequently used to calculate the finite-mass corrections, as well as the relativistic and QED corrections. In Ref. 11 the nonrelativistic wave functions were also expanded in terms of explicitly correlated Gaussians but were obtained with a finite-nuclear-mass (FNM) variational approach. Thus, the subsequently calculated relativistic corrections automatically included the finite mass effects (the so-called recoil corrections). Also, the use of the analytical energy gradient in the variational optimization of the nonlinear parameters of the Gaussians in those calculations facilitated very efficient energy minimization and produced a significantly lower Li^{-} energy than obtained by Pachucki and Komasa.[10] The maximum number of Gaussians used in the calculations was 7000. In the present work we increase this number to 10 000 and, in addition to ^{7}Li^{-}/^{7}Li calculations, we also performed ^{6}Li^{-}/^{6}Li to determine the isotope shift of the lithium electron affinity. The increase in the number of basis functions resulted in generating virtually exact (i.e., basis-set error free) nonrelativistic energies for all studied systems.

II. THE METHOD

The separation of the center-of-mass motion from the total laboratory-frame atomic nonrelativistic Hamiltonian and representing the "internal" Hamiltonian H_{int} in terms of

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Cartesian coordinates $\mathbf{r}_i$, which relate the positions of the electrons to the position of the nucleus results in the following form of H_{int}:

$$H_{\text{int}} = -\frac{1}{2}\left(\sum_{i=1}^{n}\frac{1}{\mu_i}\nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{m_0}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}\right) + \sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{i=1}^{n}\sum_{i<j}^{n}\frac{q_i q_j}{r_{ij}}, \quad (1)$$

where n is the number of the electrons in the system, $\mu_i = m_0 m_i/(m_0+m_i)$, $i=1,\ldots,n$ are the electron reduced masses $(m_i=m_e)$, q_0 is the charge of the nucleus and m_0 is its mass (12 786.3933m_e and 10 961.898m_e for ^{7}Li and ^{6}Li, respectively), and q_i, $i=1,\ldots,n$ are the electron charges.

The Gaussian basis functions used in this work to calculate the ground state energies of Li and Li$^-$ are the following:

$$\phi_k = \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}], \quad (2)$$

where $\otimes$ denotes the Kronecker product, $\mathbf{r}$ is a vector of the internal Cartesian coordinates of the electrons (for Li$^-$ $\mathbf{r}$ is a 12×1 vector and for Li $\mathbf{r}$ is a 9×1 vector), and the prime indicates the vector/matrix transposition. L_k is a lower triangular matrix of the nonlinear variation parameters. The use of the $L_k L_k'$ product in Eq. (2) instead of a single matrix allows us to vary the elements of L_k without any restrictions during the variational optimization and still ensure that each basis function is square integrable. The permutational symmetry of the electrons is implemented through appropriate symmetry projections applied to the basis functions.

As mentioned, the analytical energy gradient calculated with respect to the Gaussian nonlinear parameters (L_k) has been used in the calculations. Only the parameters of the ^{7}Li$^-$ basis set were optimized in the present work. The parameters for ^{7}Li were taken from our previous work on the Li atom[1] and in the calculations of ^{6}Li and ^{6}Li$^-$ (and of $^\infty$Li and $^\infty$Li$^-$) the parameters generated for the ^{7}Li and ^{7}Li$^-$ were used. A justification for not reoptimizing the ^{6}Li and ^{6}Li$^-$ parameters came from some earlier tests that indicated that for large basis sets, the results obtained with and without parameter reoptimizations were virtually identical.

The generation of the basis set for ^{7}Li$^-$ was done in the following manner. The size of the basis was increased incrementally by addition of subsets of twenty functions. After adding each function its nonlinear parameters (L_k) were optimized using the gradient-based procedure. After each addition of twenty functions the whole basis set was reoptimized by cycling over all functions and reoptimizing the nonlinear parameters of one basis function at a time. After the basis set was grown to the size of 10 000 functions several additional optimization cycles were performed to generate the final set.

The calculations of the relativistic effects were done in this work using the Dirac–Breit Hamiltonian in the Pauli approximation and the first-order of the perturbation theory. Thus only the relativistic effects of the order of α^2 $(\alpha=1/c)$ were accounted for. The first-order calculation of the relativistic effects usually suffices for light atoms where the velocities of the electrons are relatively low.[12,13] For the ground states (with the S symmetry) of Li and Li$^-$ the Dirac–Breit–Pauli relativistic Hamiltonian includes the mass-velocity (MV), Darwin (D), orbit-orbit (OO), and spin-spin (SS) interactions

$$H_{\text{int}}^{\text{rel}} = H_{\text{MV}} + H_{\text{D}} + H_{\text{OO}} + H_{\text{SS}}. \quad (3)$$

The formulas for the H_{MV}, H_{D}, H_{OO}, and H_{SS} operators can be found in our previous paper.[11]

As $H_{\text{int}}^{\text{rel}}$ and the nonrelativistic wave functions obtained in the finite-mass calculations and used in this work to calculate the expectation values of $H_{\text{int}}^{\text{rel}}$ depend on the mass of the nucleus, the values of the relativistic corrections depend on the isotope. We also performed the calculations of the relativistic corrections with the wave functions obtained in the infinite-mass calculations. As most of the atomic calculations are performed using the infinite-mass approximation, the infinite-mass relativistic results presented here allow a direct comparison with those calculations.

In calculating the leading QED corrections of the order α^3 and α^4 (called here E_{QED} and E_{HQED}, respectively) in this work we used the approach described in the paper by Pachucki *et al.*[10,14–16] The approach is based on the perturbation theory employed in the framework of the nonrelativistic QED method.[17–19] The zeroth-order level in this approach is the nonrelativistic Schrödiger equation. The algorithm used here was also employed in our recent work on the ground and excited states of the Be atom.[20] The α^3 and α^4 QED corrections represent the two-photon exchange, the vacuum polarization, and the electron self-energy effects. It should be emphasized that for the QED correction of the order α^4 we only determined the dominant contribution, which is the simplest to calculate. As the procedure used in this work for calculating the α^3 and α^4 QED corrections was only developed for the infinite-mass case only this type of calculations have been performed.

The numerical values of the fine structure constant and the Hartree-wave number conversion factor used in this work were taken from Ref. 21. They are the following: $\alpha = 7.297\,352\,537\,6\times 10^{-3}$ and 1 hartree $= 2.194\,746\,313\,705 \times 10^5$ cm^{-1}.

III. RESULTS

As mentioned, a basis set of 10 000 Gaussian functions was generated in this work for the ^{7}Li$^-$ ion. The ^{7}Li$^-$ results obtained with this basis, as well as with the basis sets of 7000, 8000, and 9000 basis functions, are presented in Table I. We also show the results obtained for ^{6}Li$^-$ and $^\infty$Li$^-$ and the results obtained with 10 000 basis functions for ^{6}Li, ^{7}Li, and $^\infty$Li. The results include the total nonrelativistic FNM energies (E_{nonrel}), the relativistic corrections $(E_{\text{rel}}=E_{\text{MV}}+E_{\text{D}}+E_{\text{SS}}+E_{\text{OO}})$, and the sum of the two $(E_{\text{nonrel}}+\alpha^2 E_{\text{rel}})$. As one can see, the nonrelativistic energies for all Li$^-$ isotopes are converged to within 10^{-9} hartree if not better. These energies are the lowest variational results ever obtained for ^{6}Li$^-$, ^{7}Li$^-$, and $^\infty$Li$^-$.

In the next step the Li$^-$ and Li nonrelativistic energies and the energies obtained by adding the corrections were used to calculate the ^{6}Li, ^{7}Li, and $^\infty$Li EAs. Their values are shown in Table II for basis sets ranging from 7000 to 10 000

TABLE I. Nonrelativistic energies, α^2 relativistic corrections, and the total energies for the ground states of $^{\infty}Li^-$, $^7Li^-$, $^6Li^-$, $^{\infty}Li$, ^7Li, and ^6Li. MV, D, SS, and OO are the mass-velocity, Darwin, spin-spin, and orbit-orbit corrections, respectively. $E_{rel}=E_{MV}+E_D+E_{SS}(e-e)+E_{OO}$. All values are given in hartrees.

System	Basis size	E_{nonrel}	E_{MV}	E_D	E_{SS}	E_{OO}	$E_{nonrel}+\alpha^2E_{rel}$
$^{\infty}Li^-$	7000	−7.500 776 601 5	−78.518 031	63.494 473	3.420 569	−0.431 339	−7.501 417 445 8
	8000	−7.500 776 606 3	−78.518 050	63.494 496	3.420 571	−0.431 339	−7.501 417 450 3
	9000	−7.500 776 609 7	−78.518 654	63.495 002	3.420 570	−0.431 339	−7.501 417 459 0
	10 000	−7.500 776 612 4	−78.518 663	63.495 044	3.420 559	−0.431 339	−7.501 417 460 4
	10 000[a]	−7.500 776 613 4	−78.518 651	63.495 042	3.420 559	−0.431 339	−7.501 417 460 9
$^7Li^-$	7000	−7.500 165 943 0	−78.493 053	63.479 364	3.419 805	−0.441 226	−7.500 806 828 9
	8000	−7.500 165 947 8	−78.493 072	63.479 388	3.419 807	−0.441 226	−7.500 806 833 3
	9000	−7.500 165 951 2	−78.493 676	63.479 893	3.419 806	−0.441 225	−7.500 806 842 0
	10 000	−7.500 165 953 9	−78.493 685	63.479 935	3.419 796	−0.441 225	−7.500 806 843 5
	10 000[a]	−7.500 165 954 9	−78.493 673	63.479 933	3.419 796	−0.441 225	−7.500 806 843 9
$^6Li^-$	7000	−7.500 064 316 7	−78.488 896	63.476 850	3.419 678	−0.442 870	−7.500 705 209 5
	8000	−7.500 064 321 5	−78.488 916	63.476 874	3.419 680	−0.442 870	−7.500 705 213 9
	9000	−7.500 064 324 9	−78.489 520	63.477 379	3.419 679	−0.442 870	−7.500 705 222 6
	10 000	−7.500 064 327 6	−78.489 528	63.477 421	3.419 669	−0.442 870	−7.500 705 224 1
	10 000[a]	−7.500 064 328 6	−78.489 516	63.477 419	3.419 669	−0.442 870	−7.500 705 224 5
$^{\infty}Li$	10 000	−7.478 060 323 8	−78.554 040	63.519 531	3.420 743	−0.435 598	−7.478 701 968 7
^7Li	10 000	−7.477 451 930 7	−78.529 068	63.504 432	3.419 981	−0.445 491	−7.478 093 617 3
^6Li	10 000	−7.477 350 681 2	−78.524 913	63.501 919	3.419 854	−0.447 137	−7.477 992 374 8
Literature results:							
$^{\infty}Li$ [b]	9576	−7.478 060 323 889 7					−7.478 701 998 11
$^{\infty}Li$ [b]	∞ (extrap.)	−7.478 060 323 904 1					−7.478 701 997 28
$^{\infty}Li$ [c]	∞ (extrap.)	−7.478 060 323 650 3					−7.478 701 997 67
$^{\infty}Li$ [d]	9577	−7.478 060 323 892 4					
$^{\infty}Li^-$ [e]	4200	−7.500 776 444					−7.501 417 411
$^7Li^-$ [e]	4200	−7.500 165 653					

[a]Several additional optimization cycles were performed.
[b]Reference 22.
[c]Reference 23.
[d]Reference 24.
[e]Reference 10.

functions. We also show in the table uncertainties of the EAs estimated based on the convergence of the results with the number of functions in the basis set. Based on those uncertainties we can claim that our nonrelativistic EAs values are essentially exact and the those obtained with including the relativistic corrections are converged to about 0.0030 cm^{-1}. This remaining uncertainty is almost exclusively due to the uncertainty of the relativistic correction.

The somewhat nonsmooth convergence of the relativistic corrections with the number of basis functions compared with the smooth convergence of the nonrelativistic energy is not unusual. The latter always converges more uniformly because in the variational calculation an extension of the basis set always leads to lowering of the energy. Other quantities do not usually converge as uniformly. Moreover, the dependence of the expectation values of the singular operators present in the expressions for the relativistic corrections on the local properties of the wave function is usually much stronger than that on the expectation value of the (nonsingular) nonrelativistic Hamiltonian. As the addition of new basis functions in the present calculations involved stochastic selection, some fluctuations of the local wave function behavior during the basis extension could be expected. These fluc-

TABLE II. Electron affinities (in cm^{-1}) calculated for $^{\infty}Li$, ^7Li, and ^6Li using the nonrelativistic energies and the energies obtained by adding relativistic corrections to the nonrelativistic energies. The data shown is calculated using the energy of the neutral lithium atom corresponding to the 10 000 function basis set.

Basis size	$^{\infty}Li$ (nonrel)	$^{\infty}Li$ (rel)	^7Li (nonrel)	^7Li (rel)	^6Li (nonrel)	^6Li (rel)
7000	4985.6467	4985.4710	4985.1495	4984.9737	4985.0668	4984.8910
8000	4985.6477	4985.4719	4985.1505	4984.9747	4985.0678	4984.8920
9000	4985.6485	4985.4738	4985.1513	4984.9766	4985.0686	4984.8939
10 000	4985.6491	4985.4742	4985.1519	4984.9769	4985.0692	4984.8942
10 000[a]	4985.6493	4985.4743	4985.1521	4984.9770	4985.0694	4984.8943
Remaining uncertainty	0.0010	0.0030	0.0010	0.0030	0.0010	0.0030

[a]Several additional optimization cycles were performed.

TABLE III. The Araki–Sucher term and the Bethe logarithm, as well as the total α^3 and α^4 QED corrections (denoted as $\alpha^3 E_{QED}$ and $\alpha^4 E_{HQED}$) obtained in the infinite-mass calculations with 10 000-term ground state wave function. All values are in a.u.

System	$\langle P(1/r_{ij}^3)\rangle/(4\pi)$	$\ln k_0$	$\alpha^3 E_{QED}$	$\alpha^4 E_{HQED}$
Li^- [a]	0.0242 25(10)	5.1778(2)	$1.1133(1)\times10^{-4}$	3.397×10^{-6}
Li[b]	0.0217 67(10)	5.178 16(13)	$1.113\ 611\ 4(2)\times10^{-4}$	$3.398\ 99\times10^{-6}$

[a]This work.
[b]Reference 1.

tuations are likely to affect the relativistic corrections and their convergence with the number of basis functions more than the convergence of the total energy.

The EAs calculated for different nuclear masses allow calculation of the mass effect in the EA values. Using the results obtained with 10 000 basis functions we estimate that the EA increases by 0.0827 cm^{-1} in going from ^{6}Li to ^{7}Li. The mass effects involved in the relativistic corrections give almost no contribution to this shift. The tiny difference can only be seen when six decimal digits are shown (0.082 720 cm^{-1} relativistic versus 0.082 713 cm^{-1} nonrelativistic). The EA mass shift is more pronounced for ^{7}Li and $^\infty$Li. Here the value is 0.497 193 cm^{-1} based on the nonrelativistic EAs and 0.497 233 cm^{-1} from the EAs that include relativistic corrections.

The nonrelativistic energies and the relativistic corrections calculated for the anion of the lithium atom in this work with the finite and infinite nuclear masses allow one to determine the nuclear mass effects. One can calculate these effects as differences between the respective energies of the isotopes and the INM energies. Using the energies from Table I obtained with 10 000 basis functions one gets the shifts of the nonrelativistic energy of 0.000 610 658 5 and 0.000 712 284 8 hartree between $^\infty Li^-$ and $^7Li^-$ and $^6Li^-$, respectively. The shifts for the total relativistic correction (the so-called recoil corrections) are much smaller. Their values are −0.000 000 041 5 and −0.000 000 048 4 hartree for $^7Li^-$ and $^6Li^-$ with respect to $^\infty Li^-$.

As mentioned, one of the aims of this work has been the very accurate determination of the electron affinities of $^7Li^-$ and $^6Li^-$. This goal could not be achieved without evaluating the leading QED corrections of the order of α^3 and α^4. As said, the calculations of these corrections in the present work were only performed for the case of an infinite Li nuclear mass. As such, while they provide a small contribution to the EA values, they do not contribute to the ^{7}Li/^{6}Li EA isotope shift. In the perturbation approach used to calculate the corrections we used the nonrelativistic zero-order $^\infty Li^-$ wave function expanded in terms of 10 000 Gaussians. In Table III we show the results of the calculations. Besides the corrections, for the sake of reference we also included in the table the values of $\langle P(1/r_{ij}^3)\rangle/(4\pi)$ and $\ln k_0$, which are the key components of the corrections.

The final set of results concerning the electron affinities of ^{7}Li and ^{6}Li are presented in Table IV. We show there the various contributions to the EA values and the results that include all the contributions. With those, our best estimates of the electron affinities of ^{7}Li and ^{6}Li are 4984.9842(30) and 4984.9015(30) cm^{-1}, respectively. As there is virtually no uncertainty in the nonrelativistic contributions to these two values and the uncertainty of the QED corrections we estimate to be about 0.0002 cm^{-1} (see Table III), the uncertainty of 0.0030 cm^{-1} is almost exclusively due to the inaccuracies in calculating the relativistic corrections.

There is one comment we need to make concerning the relativistic correction to the EAs of ^{7}Li. This quantity was calculated before by Pachucki and Komasa[10] and they reported the value of −0.161(5) cm^{-1}. The present calculations gave the value of −0.1751 cm^{-1}. It is unlikely that the difference between the two results is caused by the finite-mass effect which was included in our calculations but not included in theirs. The difference between the two results may appear large, but one should not forget that the results came from subtracting two quantities that are very close in magnitude. Each of these two quantities, in turn, contained a quite significant uncertainty (due to the slow convergence of the relativistic correction). This factor is likely to make the relative (but not absolute) uncertainty of the relativistic contribution to the EA quite high. In fact, the sum of the estimated uncertainties in our work of 0.003 cm^{-1} and that of Pachucki and Komasa[10] of 0.005 cm^{-1}, is of the same order of magnitude (about twice smaller, to be precise) as the difference between the result of this work and that of Ref. 10. Considering the fact that the uncertainty estimates can easily be off by a factor of two or three as there is no mathematically rigorous way to compute them (some guessing is always involved), the actual discrepancy between the two results should not be considered too concerning. This discrepancy in our view is due to the different accuracy of the two calculations.

To gain some insight on the difference between the electronic structures of $^7Li^-$ and $^6Li^-$ (and $^\infty Li^-$) we calculated some expectation values. The results of these calculations are shown in Table V. As expected, the increase in the nuclear mass results in a small reduction in the average electron-

TABLE IV. The INM, FNM, α^2 relativistic (REL), α^3 QED (QED), and α^4 QED (HQED) contributions to the electron affinities of ^{7}Li and ^{6}Li. All values are in cm^{-1}.

Contribution	^{7}Li	^{6}Li
INM	4985.6493	4985.6493
FNM	−0.4972	−0.5799
REL	−0.1751	−0.1751
QED	0.0068	0.0068
HQED	0.0004	0.0004
Total	4984.9842(30)	4984.9015(30)

TABLE V. Expectation values of interparticle distances and delta-functions dependent on interparticle distances for $^{\infty}Li^-$, $^7Li^-$, and $^6Li^-$ computed with the basis of 10 000 functions. All values are in a.u.

System	$\langle r_i \rangle$	$\langle r_{ij} \rangle$	$\langle r_i^2 \rangle$	$\langle r_{ij}^2 \rangle$	$\langle \delta(\mathbf{r}_i) \rangle$	$\langle \delta(\mathbf{r}_{ij}) \rangle$
$^{\infty}Li^-$	2.931 871 1	5.174 408 4	18.109 783	39.269 629	3.459 250	0.090 733 2
$^7Li^-$	2.932 119 5	5.174 836 8	18.112 914	39.276 174	3.458 428	0.090 712 9
$^6Li^-$	2.932 160 8	5.174 908 1	18.113 435	39.277 263	3.458 291	0.090 709 5

nucleus distance and its square ($\langle r_i \rangle$ and $\langle r_i^2 \rangle$). Also, the average interelectron distance and its square ($\langle r_{ij} \rangle$ and $\langle r_{ij}^2 \rangle$) increase slightly. Another difference between $^7Li^-$ and $^6Li^-$ one can see in the value of the electron-nucleus and electron-electron contact terms ($\langle \delta_i \rangle$ and $\langle \delta_{ij} \rangle$). Both of them decrease slightly in going from $^6Li^-$ to $^7Li^-$.

IV. SUMMARY

There have been two goals in this work. The first was to obtain nearly basis-set-error free total finite-mass energies of the lithium anion isotopes and the second was to calculate with very high accuracy their electron affinities and the isotope shift between the EAs of ^6Li and ^7Li. The value of the shift obtained in the calculations of 0.0827 cm^{-1} is large enough to be measured experimentally. Such a measurement would provide an excellent test of the theoretical model used in the calculations presented in this work.

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