Electron affinity of ^{7}Li calculated with the inclusion of nuclear motion and relativistic corrections

Monika Stanke
Department of Chemistry, University of Arizona, Tucson, Arizona 85721 and Institute of Physics, Nicholas Copernicus University, ulica Grudziadzka 5, PL 87-100 Toruń, Poland

Dariusz Kędziera
Department of Chemistry, Nicholas Copernicus University, ulica Gagarina 7, PL 87-100 Toruń, Poland

Sergiy Bubin
Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Ludwik Adamowicz
Department of Chemistry, University of Arizona, Tucson, Arizona 85721 and Department of Physics, University of Arizona, Tucson, Arizona 85721

Explicitly correlated Gaussian functions have been used to perform very accurate variational calculations for the ground states of ^{7}Li and ^{7}Li$^-$. The nuclear motion has been explicitly included in the calculations (i.e., they have been done without assuming the Born-Oppenheimer (BO) approximation). An approach based on the analytical energy gradient calculated with respect to the Gaussian exponential parameters was employed. This led to a noticeable improvement of the previously determined variational upper bound to the nonrelativistic energy of Li$^-$. The Li energy obtained in the calculations matches those of the most accurate results obtained with Hylleraas functions. The finite-mass (non-BO) wave functions were used to calculate the α^2 relativistic corrections ($\alpha = 1/c$). With those corrections and the α^3 and α^4 corrections taken from Pachucki and Komasa [J. Chem. Phys. **125**, 204304 (2006)], the electron affinity (EA) of ^{7}Li was determined. It agrees very well with the most recent experimental EA. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2755767]

I. INTRODUCTION

In a recent work[1] Pachucki and Komasa reported new variational infinite-mass (Born-Oppenheimer) calculations of the ground electronic states of Li$^-$ and Li performed with the use of explicitly correlated Gaussian functions (ECGFs). They also calculated the corrections due to the finite mass of the ^{7}Li nucleus, as well as relativistic and QED corrections proportional to α^2, α^3, and α^4. While the variational infinite-mass energy of Li that they obtained was slightly higher than the best variational upper bound of −7.478 060 323 889 7 hartrees,[2] their result for Li$^-$ was a new energy upper bound. In the summary of their paper, Pachucki and Komasa stated that this new upper bound can still be lowered if a better optimized basis set is used in the calculation. Such an improvement may affect the electron affinity (EA) of Li that they calculated in their work. Since in the last years we have developed an approach for variational optimization of ECGFs based on the use of the analytical energy gradient with respect to the Gaussian exponential parameters, we decided to revisit the Li$^-$/Li problem to see if the ECGF results for these systems can be improved.

Although the basis functions (ECGFs) used in our work are the same as those employed by Pachucki and Komasa in Ref. 1, our approach differs from the approach used in Ref. 1 in three aspects. First, we do not assume the infinite-mass approximation in the calculations, and all particles (the elec-

trons and the nucleus) forming the ^{7}Li$^-$ ion and the ^{7}Li atom are treated on equal footing. Thus, the finite-mass corrections, which in the work of Pachucki and Komasa were calculated using the first-order perturbation theory, in our approach are explicitly included in the variational nonrelativistic energy. Second, as mentioned above, we use the analytic gradient of the energy with respect to the Gaussian exponential parameters in the variational optimizations of the wave functions. Third, the α^2 relativistic corrections in the present work are determined using the finite-mass wave functions, and thus those corrections include not only terms due to the motion of the electrons around the center of mass of the atom but also terms due to the motion of the nucleus. The calculations of the relativistic correction were carried out using recently developed algorithms.[3–7]

The most accurate atomic calculations for systems with two and three electrons have been done with Slater-type or Hylleraas-type explicitly correlated functions.[2,8–11] Those calculations demonstrated that by accurately accounting for the electron correlation effects and by including the leading relativistic and QED corrections, the accuracy of the results of the calculations matches the accuracy of the state-of-the-art high-resolution experiment. The Slater-type and Hylleraas-type functions are more effective than ECGFs in describing the cusp behavior of the wave function, but their implementation to systems with more than three electrons has not been achieved due to technical difficulties related to

calculating the matrix elements. This presently makes the ECGFs the only viable alternative for very accurate calculation of atoms with more than three electrons.

While our works employing ECGFs have focused on small molecular systems,[12–18] there have been works done with those functions on small atoms.[1,19–21] Recently we have joined this effort with works on ^{3}He and ^{4}He (Ref. [3]) and on ^{9}Be and ^{9}Be$^+$,[5,6] where we showed that by using an extended basis set and by employing a gradient-based variational optimization of the Gaussian parameters, we can achieve a very high accuracy in variational calculations with ECGFs. In this work we apply the approach to the Li/Li$^-$ system.

II. METHOD USED IN THE CALCULATIONS

Li and Li$^-$ are four- and five-particle problems, respectively, for an approach that does not assume the infinite-mass approximation. In general, for a system of N particles with masses M_i and charges Q_i ($i=1,\ldots,N$) the approach that we use comprises the following steps. In the first step we transform the total nonrelativistic Hamiltonian of the system to an internal Hamiltonian by separating out the center of mass motion. This reduces the N-particle problem to a n-pseudoparticle problem ($n=N-1$). In the transformation the laboratory Cartesian coordinate system is replaced by a system, whose first three coordinates are the laboratory coordinates of the center of mass $\mathbf{r}_0$, and the remaining $3n$ coordinates are internal Cartesian coordinates, whose origin is placed at the nucleus (called the reference particle). The positions of the other particles (electrons) are described using the Cartesian position vectors $\mathbf{r}_i$. The internal Hamiltonian H_{int} has the following form:

$$H_{\text{int}} = -\frac{1}{2}\left(\sum_{i=1}^{n}\frac{1}{\mu_i}\nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{M_1}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}\right)$$
$$+ \sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{i=1}^{n}\sum_{i<j}^{n}\frac{q_i q_j}{r_{ij}}, \tag{1}$$

where $\mu_i = M_1 M_{i+1}/(M_1+M_{i+1})$ are reduced masses. The separation of the total Hamiltonian into the internal Hamiltonian and the Hamiltonian of the motion of the center of mass is exact. One can notice that H_{int} represents a system of n pseudoparticles (pseudoelectrons) with charges $q_i=Q_{i+1}$ and reduced masses μ_i moving in the central potential of the charge of the reference particle. We call the internal particles as pseudoparticles because, while they have the same charges as the original particles, their masses are replaced by the reduced masses. For Li, the number of pseudoparticles is 3 and for Li$^-$ it is 4.

To describe the relativistic effects in ^{7}Li and ^{7}Li$^-$, we use the Dirac-Breit Hamiltonian in the Pauli approximation, which suffices for light atoms where the velocities of the electrons are relatively low.[22,23] In this work we only consider the ground states of Li and Li$^-$. Those states have the S symmetry. For such states the Dirac-Breit-Pauli Hamiltonian has the following form:

$$H_{\text{int}}^{\text{rel}} = H_{\text{MV}} + H_{\text{D}} + H_{\text{OO}} + H_{\text{SS}}, \tag{2}$$

where

mass-velocity term:

$$H_{\text{MV}} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{4}\nabla_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{4}\frac{1}{m_i^3}\nabla_{\mathbf{r}_i}^4\right],$$

Darwin term:

$$H_{\text{D}} = -\frac{\pi}{2}\left[\sum_{i=1}^{4}\frac{1}{m_i^2}q_0 q_i\delta^3(r_i) + \sum_{i=1}^{4}\sum_{j=1,j\neq i}^{4}\frac{1}{m_i^2}q_i q_j\delta^3(r_{ij})\right]$$
$$+ \frac{14\pi}{3}\sum_{i=1}^{4}\frac{1}{m_0^2}q_0 q_i\delta^3(r_i),$$

orbit-orbit term:

$$H_{\text{OO}} = -\frac{1}{2}\sum_{i=1}^{4}\sum_{j=1}^{4}\frac{q_0 q_i}{m_0 m_i}\left[\frac{1}{r_i}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j} + \frac{1}{r_i^3}\mathbf{r}_i\cdot(\mathbf{r}_i\cdot\nabla_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right]$$
$$+ \frac{1}{2}\sum_{i=1}^{3}\sum_{j>i}^{4}\frac{q_i q_j}{m_i m_j}\left[\frac{1}{r_{ij}}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}\right.$$
$$+ \left.\frac{1}{r_{ij}^3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\nabla_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right],$$

spin-spin term:

$$H_{\text{SS}} = -\frac{8\pi}{3}\sum_{i=1}^{4}\frac{q_0 q_i}{m_0 m_i}(\mathbf{S}_0\cdot\mathbf{S}_i)\delta^3(r_i)$$
$$- \frac{8\pi}{3}\sum_{j=1}^{4}\sum_{i>j}^{4}\frac{q_i q_j}{m_i m_j}(\mathbf{S}_i\cdot\mathbf{S}_j)\delta^3(r_{ij}).$$

For ^{7}Li in a.u., $q_0=Q_1=3$, $q_1=Q_2=-1$, $q_2=Q_3=-1$, $q_3=Q_4=-1$, $m_0=M_1=12\,786.3933$, $m_1=M_2=1$, $m_2=M_3=1$, and $m_3=M_4=1$. Additionally for ^{7}Li$^-$, $q_4=Q_5=-1$ and $m_4=M_5=1$. In this work we do not consider the electron-nucleus spin-spin interaction because it is a negligibly small effect in comparison with the electron-electron spin-spin interaction.

Since both ^{7}Li and ^{7}Li$^-$ have a nucleus with spin of 3/2, this needs to be taken into consideration in the calculation. In the atomic Dirac-Breit-Pauli Hamiltonian the Darwin correction describing the interaction of the nucleus (with charge Q, spin I, and mass M) with an electron has the following form:[24]

$$\frac{2\pi}{3}\frac{Q}{M^2}(g-1)|(1+\zeta)\delta^3(r),$$

where g is the g factor (for ^{7}Li nucleus it is 2.170 951), and

$$\zeta = \begin{cases} 0 & \text{for an integer spin,} \\ \dfrac{1}{4I} & \text{for a half-integer spin.} \end{cases} \tag{3}$$

The general form of the basis functions used in this work to calculate the ^{7}Li and ^{7}Li$^-$ S states is

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

System	Basis	E_{nonrel}	$\alpha^2 E_{\mathrm{MV}}$	$\alpha^2 E_{\mathrm{D}}$	$\alpha^2 E_{\mathrm{SS}}(e-e)$	$\alpha^2 E_{\mathrm{OO}}$	$\alpha^2 E_{\mathrm{rel}}$	$E_{\mathrm{nonrel}}+\alpha^2 E_{\mathrm{rel}}$
$^\infty$Li$^-$	1000	−7.500 774 663 3	−4.178 131 1	3.378 095 9	0.182 326 4	−0.022 969 4	−0.640 678 1	−7.501 415 341 4
	1500	−7.500 776 032 5	−4.180 456 8	3.380 252 6	0.182 229 2	−0.022 969 4	−0.640 944 4	−7.501 416 976 8
	2000	−7.500 776 375 6	−4.180 558 2	3.380 438 9	0.182 219 1	−0.022 969 4	−0.640 869 6	−7.501 417 245 3
	2500	−7.500 776 488 8	−4.180 884 9	3.380 803 9	0.182 169 2	−0.022 969 4	−0.640 881 1	−7.501 417 370 0
	3000	−7.500 776 526 1	−4.181 031 9	3.380 963 3	0.182 166 4	−0.022 969 4	−0.640 871 7	−7.501 417 397 8
	3500	−7.500 776 551 7	−4.181 026 5	3.380 973 2	0.182 158 8	−0.022 969 4	−0.640 863 9	−7.501 417 415 6
	4000	−7.500 776 567 4	−4.181 062 8	3.380 998 1	0.182 156 0	−0.022 969 4	−0.640 878 2	−7.501 417 445 6
	4500	−7.500 776 577 5	−4.181 052 5	3.381 006 2	0.182 155 5	−0.022 969 4	−0.640 860 2	−7.501 417 437 8
	5000	−7.500 776 584 8	−4.181 044 7	3.381 014 9	0.182 154 3	−0.022 969 4	−0.640 844 9	−7.501 417 429 7
	6000	−7.500 776 594 8	−4.181 187 1	3.381 149 3	0.182 154 1	−0.022 969 4	−0.640 853 1	−7.501 417 447 9
	7000	−7.500 776 601 2	−4.181 186 8	3.381 150 9	0.182 153 8	−0.022 969 4	−0.640 851 5	−7.501 417 452 7
$^\infty$Li	1000	−7.478 060 276 4	−4.182 690 0	3.381 984 6	0.182 215 5	−0.023 196 2	−0.641 686 1	−7.478 701 962 4
	1500	−7.478 060 305 5	−4.182 726 7	3.382 094 6	0.182 211 3	−0.023 196 2	−0.641 616 9	−7.478 701 922 5
	2000	−7.478 060 313 5	−4.182 953 4	3.382 294 9	0.182 211 1	−0.023 196 2	−0.641 643 5	−7.478 701 957 1
	2500	−7.478 060 317 1	−4.182 950 4	3.382 306 1	0.182 198 9	−0.023 196 2	−0.641 641 6	−7.478 701 958 7
	3000	−7.478 060 319 0	−4.182 987 7	3.382 372 4	0.182 196 4	−0.023 196 2	−0.641 615 1	−7.478 701 934 1
	3500	−7.478 060 319 9	−4.182 998 2	3.382 383 6	0.182 192 4	−0.023 196 2	−0.641 618 3	−7.478 701 938 3
	4000	−7.478 060 320 9	−4.183 000 2	3.382 385 8	0.182 192 5	−0.023 196 2	−0.641 618 1	−7.478 701 939 0
	4500	−7.478 060 321 6	−4.183 002 1	3.382 388 2	0.182 190 2	−0.023 196 2	−0.641 619 9	−7.478 701 941 5
	5000	−7.478 060 322 1	−4.183 002 1	3.382 389 7	0.182 186 9	−0.023 196 2	−0.641 621 7	−7.478 701 943 8
	6000	−7.478 060 322 8	−4.183 037 4	3.382 424 9	0.182 182 9	−0.023 196 2	−0.641 625 7	−7.478 701 948 6
	7000	−7.478 060 323 2	−4.183 031 4	3.382 423 0	0.182 177 2	−0.023 196 2	−0.641 627 4	−7.478 701 950 7
^{7}Li$^-$	1000	−7.500 164 005 3	−4.176 801 9	3.377 292 0	0.182 285 7	−0.023 496 0	−0.640 720 1	−7.500 804 725 5
	1500	−7.500 165 374 2	−4.179 126 9	3.379 448 3	0.182 188 5	−0.023 495 9	−0.640 986 0	−7.500 806 360 3
	2000	−7.500 165 717 3	−4.179 228 3	3.379 634 6	0.182 178 4	−0.023 495 9	−0.640 911 2	−7.500 806 628 6
	2500	−7.500 165 830 5	−4.179 554 9	3.379 999 5	0.182 128 6	−0.023 495 9	−0.640 922 7	−7.500 806 753 2
	3000	−7.500 165 867 7	−4.179 701 9	3.380 158 8	0.182 125 7	−0.023 495 9	−0.640 913 2	−7.500 806 781 0
	3500	−7.500 165 893 3	−4.179 696 5	3.380 168 7	0.182 118 1	−0.023 495 9	−0.640 905 5	−7.500 806 798 8
	4000	−7.500 165 909 0	−4.179 732 8	3.380 193 7	0.182 115 3	−0.023 495 9	−0.640 919 7	−7.500 806 828 7
	4500	−7.500 165 919 1	−4.179 722 5	3.380 201 7	0.182 114 8	−0.023 495 9	−0.640 901 8	−7.500 806 820 9
	5000	−7.500 165 926 3	−4.179 714 7	3.380 210 5	0.182 113 6	−0.023 495 9	−0.640 886 5	−7.500 806 812 8
	6000	−7.500 165 936 3	−4.179 857 1	3.380 344 8	0.182 113 4	−0.023 495 9	−0.640 894 7	−7.500 806 831 0
	7000	−7.500 165 942 7	−4.179 856 8	3.380 346 5	0.182 113 1	−0.023 495 9	−0.640 893 1	−7.500 806 835 8
^{7}Li	1000	−7.477 451 883 3	−4.181 360 4	3.381 180 7	0.182 174 9	−0.023 723 0	−0.641 727 9	−7.478 093 611 2
	1500	−7.477 451 912 5	−4.181 397 0	3.381 290 6	0.182 170 7	−0.023 723 0	−0.641 658 7	−7.478 093 571 1
	2000	−7.477 451 920 4	−4.181 623 7	3.381 490 9	0.182 170 5	−0.023 723 0	−0.641 685 3	−7.478 093 605 7
	2500	−7.477 451 924 0	−4.181 620 7	3.381 502 1	0.182 158 3	−0.023 723 0	−0.641 683 3	−7.478 093 607 3
	3000	−7.477 451 925 8	−4.181 658 0	3.381 568 3	0.182 155 8	−0.023 723 0	−0.641 656 9	−7.478 093 582 7
	3500	−7.477 451 926 8	−4.181 668 4	3.381 579 6	0.182 151 8	−0.023 723 0	−0.641 660 1	−7.478 093 586 9
	4000	−7.477 451 927 7	−4.181 670 5	3.381 581 8	0.182 151 9	−0.023 723 0	−0.641 659 9	−7.478 093 587 6
	4500	−7.477 451 928 4	−4.181 672 4	3.381 584 1	0.182 149 6	−0.023 723 0	−0.641 661 6	−7.478 093 590 1
	5000	−7.477 451 929 0	−4.181 672 4	3.381 585 7	0.182 146 3	−0.023 723 0	−0.641 663 4	−7.478 093 592 4
	6000	−7.477 451 929 7	−4.181 707 6	3.381 620 9	0.182 142 3	−0.023 723 0	−0.641 667 5	−7.478 093 597 1
	7000	−7.477 451 930 1	−4.181 701 7	3.381 619 0	0.182 136 6	−0.023 723 0	−0.641 669 2	−7.478 093 599 3

$$\phi_k = \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}], \qquad (4)$$

where $\otimes$ is the Kronecker product symbol, $\mathbf{r}$ is a vector of the internal Cartesian coordinates of the four pseudoparticles (for ^{7}Li$^-$ $\mathbf{r}$ is a 12×1 vector, for ^{7}Li $\mathbf{r}$ is a 9×1 vector), L_k is the lower triangular matrix of nonlinear variation parameters (for ^{7}Li$^-$ L_k is a 4×4 rank 4 matrix and for ^{7}Li L_k is a 3×3 rank 3 matrix), and I_3 is the 3×3 identity matrix. The use of the $L_k L_k'$ product instead of a single matrix allows us to vary the L_k without any restrictions and still ensure that

each basis function is square integrable. The permutational symmetry of the two electrons is implemented through appropriate symmetry projections applied to the basis functions.

As in our previous non-Born-Oppenheimer calculations on atomic and diatomic systems, the wave functions for the ground states of ^{7}Li and ^{7}Li$^-$ have been obtained using the variational method by minimizing the total energy with respect to the linear expansion coefficients $\{c_k\}$ and the nonlinear parameters of the basis functions $\{L_k\}$. In the minimiza-

TABLE II. Contributions to the electron affinity of ^{7}Li: comparison of the values obtained in this work with those of Pachucki and Komasa (Ref. [1])

Contribution type	Li$^-$ (hartree)[a]	Li (hartree)[a]	EA (cm^{-1})[a]	Li$^-$ (hartree)[b]	Li (hartree)[b]	EA (cm^{-1})[b]
E_{nonrel}	−7.500 165 943	−7.477 451 930	4985.1495	−7.500 776 444	−7.478 060 320	4985.61(18)
E_{FM}	0.000 610 658[c]	0.000 608 393[c]	−0.4972	0.000 610 791	0.000 608 525	−0.497(0)
$\alpha^2 E_{rel}$	−0.000 640 893	−0.000 641 669	−0.1703	−0.000 640 967	−0.000 641 703	−0.161(5)
$\alpha^3 E_{QED}^{(3)}$			0.0072	0.000 111 328	0.000 111 361	0.007(0)
$\alpha^4 E_{QED}^{(4)}$			0.0002	0.000 003 397	0.000 003 398	0.000(0)
E_{total}	−7.500 692 111[d]	−7.477 978 840[d]	4984.9867	−7.500 691 895	−7.477 978 739	4984.96(18)

[a]This work. Our E_{nonrel} includes the finite-mass contribution.
[b]Reference [1].
[c]The finite-mass correction. We computed this value as the difference between our finite-mass and infinite-mass nonrelativistic energies, In Ref. [1] this was computed with the perturbation theory.
[d]This energy includes the $\alpha^3 E_{QED}^{(3)}$ and $\alpha^4 E_{QED}^{(4)}$ corrections taken from Ref. [1].

tion we used analytically determined energy gradient. The use of the gradient significantly accelerated the optimization process and allowed us to achieve a high accuracy of the calculations at a lower computational cost.

III. RESULTS

The results of the calculations of the nonrelativistic energies and relativistic corrections are summarized in Table I. In the table we show how these quantities converge with the number of basis functions. Results from 1000 to 7000 basis functions in increments of 1000 are shown. Since all previous calculations on Li and Li$^-$, including those of Pachucki and Komasa,[1] have been done for an infinite nuclear mass, we also show in the table infinite-mass energies. These energies were calculated using the basis set obtained for ^{7}Li and ^{7}Li$^-$, and no additional optimizations of the nonlinear parameters were performed. Our previous calculations on atomic systems have shown that adjusting only linear parameters $\{c_k\}$ is sufficient to account for a change of the nuclear mass from its finite value of 12 786.3933 hartrees to infinity.

The infinite-mass energy results (denoted as $^\infty$Li and $^\infty$Li$^-$ in Table I) obtained in our calculations can be directly compared with the recent results by Pachucki and Komasa.[1] Our $^\infty$Li$^-$ variational energy obtained with 7000 basis functions of −7.500 776 601 2 hartrees is noticeably lower than their result of −7.500 776 444 hartrees. The improvement is much smaller for $^\infty$Li. Here our energy obtained with 7000 basis functions is −7.478 060 323 2 hartrees and their result is −7.478 060 320 hartrees. We should add that the best variational energy for Li of −7.478 060 323 889 7 hartrees was recently obtained with Hylleraas-type basis functions by Puchalski and Pachucki.[2]

The convergence of the total variational energy with the number of basis functions is faster for Li than for Li$^-$. Going from 6000 to 7000 basis functions, the Li$^-$ energy decreased by 6×10^{-9} hartree, while the Li energy decreased by only 4×10^{-10} hartree. This is expected due to the larger by one number of electrons in Li$^-$ than in Li. In effect, when the electron affinity of Li is calculated as a difference of the total relativistic energies of Li and Li$^-$ plus the difference of the relativistic corrections, the results should be an upper bound to the true EA value.

In Table I we also show all individual relativistic energy corrections of the order of α^2 calculated in this work using

our finite-mass wave functions and the first-order perturbation theory. The sums of those corrections added to the non-relativistic total energies are shown in the last column of the table ($E_{nonrel} + \alpha^2 E_{rel}$). As one can see, the convergence of $\alpha^2 E_{rel}$ is quite good, however, not as good as for the total nonrelativistic energy. Our α^2 relativistic corrections for ^{7}Li and $^\infty$Li, calculated with the 7000-term wave functions, of −0.000 641 669 and −0.000 641 627 hartree, respectively, can be compared with the α^2 correction equal to −0.000 641 703 hartree obtained with the infinite-mass wave function by Pachucki and Komasa.[19] The values are very similar but not identical.

In Table II we present the calculation of EA of Li using the energies obtained in this work with 7000 basis functions, and we compare it with the calculation of Pachucki and Komasa.[1] In the first row of the table we list our finite-mass total energies of ^{7}Li and ^{7}Li$^-$ and the infinite-mass energies of Pachucki and Komasa. The second row contains finite-mass corrections (E_{FM}) for the two systems. While in our approach those corrections are calculated as the difference between the corresponding finite-mass and infinite-mass total energies, in the approach used by Pachucki and Komasa they are calculated as perturbations to the infinite-mass energies. As one can see, our E_{FM} corrections for both systems are slightly smaller than theirs and the difference is about 0.02%. However, the difference between E_{FM} for Li and Li$^-$, i.e., the contribution of the finite-mass effect to the EA of Li, is virtually identical in our calculations as was in the calculations of Pachucki and Komasa.

Slightly larger differences of about 0.036 and 0.009 cm^{-1} between our results and those of Pachucki and Komasa appear in the contribution to the EA from the non-relativistic energies and from the α^2 relativistic corrections. The former is the result of Pachucki and Komasa for Li$^-$ energy being not as well converged as our energy. The latter may result from our use of the non-Born-Oppenheimer (BO) wave functions in calculating the relativistic corrections and their use of BO wave functions.

Since we have not computed QED corrections of the orders of α^3 and α^4 and Pachucki and Komasa did, we used their values to get our final EA result. The QED corrections are very small in this case and contribute less than 0.01 cm^{-1} to the EA value. With those corrections, our EA of Li equals to 4984.9867 cm^{-1}. This result agrees very well with the EA

TABLE III. Convergence of the electron affinity for ^{7}Li. The computed values include α^3 and α^4 QED corrections taken from Pachucki and Komasa (Ref. [1]).

Basis	EA (cm^{-1})
1000	4984.5209
2000	4984.9398
3000	4984.9783
4000	4984.9877
5000	4984.9831
6000	4984.9861
7000	4984.9867
Ref. [1]	4984.96(18)
Expt. (Ref. [25])	4984.90(17)

of 4984.96(18) cm^{-1} by Pachucki and Komasa as well as with the most recent experimental value of 4984.90(17) cm^{-1}.[25]

Finally, we found that it interesting to examine how the EA converges with the number of functions in the basis set. The pertinent information is presented in Table III. As one can see, the EA value is already well converged with 3000–4000 basis functions.

IV. SUMMARY

In this work we have presented a series of calculations leading to the determination of the electron affinity of the Li atom. The calculations have been done without assuming the Born-Oppenheimer approximation regarding the separability of the electronic and nuclear motions (i.e., with the inclusion of the nuclear motion in the nonrelativistic Schrödinger equation). In this work we differ with the approach employed earlier by Pachucki and Komasa,[1] where they first calculated nonrelativistic infinite-nuclear-mass energies and then corrected them for the finite mass of the Li nucleus using the perturbation theory. By recalculating the Li and Li$^-$ ground-state energies with an infinite mass of the nucleus, we obtained energy values that we could compare directly with the infinite-mass energies obtained by Pachucki and Komasa. The comparison showed that our nonrelativistic energies are better converged (particularly for Li$^-$) than theirs. Our Li$^-$ infinite-mass and finite-mass energies are new improved upper bounds for this system. In the next step we calculated the relativistic corrections of the order of α^2 to the ^{7}Li and ^{7}Li$^-$ energies using our nonrelativistic finite-mass wave functions. The difference between the Li/Li$^-$ nonrelativistic energies,

plus the difference between the relativistic corrections, gave us the initial EA value. To obtain the final EA value we added the QED corrections calculated by Pachucki and Komasa to our result. The value of EA we got agrees well with the most recent experimental result of Haeffler *et al.*[25]

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