Electron affinity of ^{7}Li

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Abstract

Variationally optimized exponentially correlated Gaussian (ECG) functions are employed to obtain nonrelativistic wave functions of the Lithium atom and its negative ion. The energy levels are computed by means of the expansion in powers of the fine-structure constant α. The first term of this expansion corresponds to the nonrelativistic energy. The higher order terms represent the relativistic and radiative corrections and are determined by some effective Hamiltonians. Highly accurate expectation values of singular operators entering these Hamiltonians are computed using a set of expectation value identities. The resulting electron affinity of Lithium atom 4984.96(18) cm^{-1} agrees very well with 4984.90(17) cm^{-1} of the latest measurements.

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I. INTRODUCTION

The continuous interaction between theory and experiment in providing results of increasing accuracy enables mutual verification of the outcome and supports development of new methods. For many years, such a stimulating interplay between theory and experiment has been observed in the area of one- [1, 2] and two-electron [3–6] atoms. Many useful benchmarks and methodologies have been established, and unquestionable contribution to the refinement of the fundamental constants comes from this area. Precision of theoretical predictions is often comparable with that of the measurements [1]. The difference between the results obtained in the high precision computations and the measured ones can be used to extract higher order effects or even discover new subtle phenomena [7]. For instance, the tiny field shift effect resulting from the spatial nuclear charge distribution can be studied quantitatively providing the information on the size of the nucleus [8, 9].

Our goal is to transfer the experience and the knowledge gained in the area of high precision computations for one- and two-electron atoms to slightly larger systems—atoms and molecules with a few electrons. A condition *sin equa non* of preserving high accuracy of the computations is the ability to construct a multielectron, fully correlated, non-relativistic wave function. While for two electron systems [10–13] as well as for the lithium atom [14, 15] solving the Schrödinger equation to an accuracy of 10 or more significant figures is achievable using several methods, for larger systems such an accuracy is still a challenging issue. Nevertheless, the clamped nuclei nonrelativistic energy accurate to 7-8 significant figures has been obtained for the four-electron atoms and molecules. The method able to reach such an accuracy relies on expansion of the wave function in the basis of multielectron exponentially correlated Gaussian (ECG) functions [16].

Before a meaningful comparison between theory and experiment can be made, the relativistic and the quantum electrodynamics (QED) corrections must be incorporated into the theoretical model. For small systems consisting of light nuclei the presently most reliable approach is based on the expansion of the energy in powers of the fine structure constant α [17]

$$E(\alpha) = \sum_{i=0} E^{(i)}. \tag{1}$$

The coefficients $E^{(i)}$ are proportional to α^i and are expressed as the expectation values of some effective Hamiltonians with the nonrelativistic wave function. These Hamiltonians can be derived in frames of the nonrelativistic quantum electrodynamics and the leading terms of the expansion (1) have been known since early work by Bethe and Salpeter [18], Araki [19], and Sucher [20]. The leading terms of the expansion can be given a transparent physical interpretation. $E^{(0)} \equiv E_{\rm NR}$ is the nonrelativistic energy found as a solution to the electronic Schrödinger equation. The $E^{(1)}$ term is absent and the $E^{(2)} \equiv \alpha^2 E_{\rm REL}$ coefficient determines the leading relativistic correction evaluated as the expectations value of the Breit-Pauli Hamiltonian. The $E^{(3)} \equiv \alpha^3 E_{\rm QED}$ term is the leading QED correction whose precise determination is indispensable in high accuracy calculations. Quite recently, an explicit form of the higher order QED correction $E^{(4)} \equiv \alpha^4 E_{\rm HQED}$ has also been found [21, 22]. Precise evaluation of these leading corrections for the ground states of Lithium anion and Lithium neutral atom is the main subject of the present work. An adequacy of this approach will be verified by a comparison of the computed electron affinity (EA) of Lithium with that determined experimentally.

II. THE METHOD

Particular form of the coefficients of the α-expansion of the energy, valid for the S-state atoms, is given below. $E_{\rm NR}$ is a sum of E_0, the solution of the Schrödinger equation $H_0\Psi = E_0\Psi$ with the clamped nuclei Hamiltonian

$$H_0 = -\sum_i \left(\frac{\boldsymbol{\nabla}_i^2}{2} + \frac{Z}{r_i}\right) + \sum_{i>j} \frac{1}{r_{ij}}\,, \tag{2}$$

the finite nuclear mass correction

$$E_{\rm FM} = \frac{1}{2M} \left\langle \Psi \left| \left(\sum_i \boldsymbol{\nabla}_i\right)^2 \right| \Psi \right\rangle, \tag{3}$$

and higher order $\mathcal{O}(1/M^2)$ terms which are neglected here. Similarily, the recoil contributions, i.e. the α^2/M and α^3/M terms, to the remaining α-expansion terms have been neglected as numerically small.

The leading relativistic correction coefficient $E_{\rm REL}$ is given by the expectation value of the Breit-Pauli Hamiltonian, which in the nonrecoil limit and for the case of the S-state atom simplifies to

$$H_{\mathrm{REL}} = \sum_i \left[-\frac{\boldsymbol{\nabla}_i^4}{8} + \frac{Z\pi}{2}\,\delta(\boldsymbol{r}_i)\right] + \sum_{i>j} \pi\,\delta(\boldsymbol{r}_{ij}) \quad (4)$$
$$+ \sum_{i>j} \frac{1}{2}\left(\frac{1}{r_{ij}}\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j + \frac{1}{r_{ij}^3}\boldsymbol{r}_{ij}\cdot(\boldsymbol{r}_{ij}\cdot\boldsymbol{\nabla}_i)\,\boldsymbol{\nabla}_j\right).$$

The hyperfine splitting term is also omitted here—for ^{7}Li this contribution is below 0.03 cm^{-1} [23] and for the closed shell Li$^-$ vanishes by symmetry.

The next coefficient of the expansion (1), E_{QED}, describes the leading QED correction which accounts for the physical effects of the two photon exchange, vacuum polarization, electron self-energy, etc.

$$\begin{aligned} E_{\mathrm{QED}} &= \sum_{i>j}\left\{\left[\frac{164}{15} + \frac{14}{3}\ln\alpha\right]\langle\Psi\,|\delta(\boldsymbol{r}_{ij})|\,\Psi\rangle \right. \\ &\left. -\frac{14}{3}\left\langle\Psi\left|\frac{1}{4\pi}\,P\left(\frac{1}{r_{ij}^3}\right)\right|\Psi\right\rangle\right\} \\ &+ \sum_i\left[\frac{19}{30} + \ln(\alpha^{-2}) - \ln k_0\right]\frac{4Z}{3}\,\langle\Psi\,|\delta(\boldsymbol{r}_i)|\,\Psi\rangle\,, \end{aligned} \quad (5)$$

where also the recoil contributions were omitted. The expression above contains the so called Araki-Sucher term

$$\left\langle\phi\left|P\left(\frac{1}{r^3}\right)\right|\psi\right\rangle \equiv \quad (6)$$
$$\lim_{a\to 0}\int \phi^*(\boldsymbol{r})\,\psi(\boldsymbol{r})\left[\frac{1}{r^3}\,\Theta(r-a) + 4\,\pi\,\delta(\boldsymbol{r})\,(\gamma + \ln a)\right]d\boldsymbol{r},$$

with Θ being the step function and γ – the Euler constant, and the many-electron Bethe logarithm $\ln k_0$, which can be defined as

$$\ln k_0 = -\frac{1}{D}\,\langle\Psi|\boldsymbol{\nabla}\,(H_0 - E_0)\,\ln\!\big[2\,(H_0 - E_0)\big]\,\boldsymbol{\nabla}\,|\Psi\rangle, \quad (7)$$

with the following symbols used

$$\boldsymbol{\nabla} = \sum_i \boldsymbol{\nabla}_i\,, \quad (8)$$
$$D = 2\,\pi\,Z\left\langle\Psi\left|\sum_i \delta(\boldsymbol{r}_i)\right|\Psi\right\rangle. \quad (9)$$

The higher order term proportional to α^4 is quite complicated [21]. For its numerical contribution to the total energy is small, we approximate it by the leading one-loop correction

$$E_{\mathrm{HQED}} \approx 4\,\pi\,Z^2\left(\frac{139}{128} + \frac{5}{192} - \frac{\ln(2)}{2}\right)\,\langle\Psi|\sum_{ij}\delta(\boldsymbol{r}_i)|\Psi\rangle. \quad (10)$$

The remaining α^4 contributions involve singular terms which are relatively difficult to compute and require special treatment [5, 22]. The approximate value of the $E^{(4)}$ component gives a rough estimate of the error made by cutting off the expansion (1).

The formulas presented in this Section make the basis for practical calculations. To perform successfully such calculations we must address the following three issues. The first and the most important issue that arises is how to generate the nonrelativistic wave function with full correlation included. Next, we have to find a way to accurately compute the singular operators $\delta(\mathbf{r}_i)$, $\delta(\mathbf{r}_{ij})$, ∇_i^4, and $P(1/r_{ij}^3)$. Finally, to have the α^3 term completed, we need an algorithm to accurately compute the Bethe logarithms. Below, we are going to show what we can do about these three issues.

III. THE NONRELATIVISTIC WAVE FUNCTION

Our ansatz for the nonrelativistic wave function is represented by a K-term linear combination of n-electron spatial basis functions $\{\psi_l(\boldsymbol{r})\}$ multiplied by an appropriate spin eigenfunction, Ξ_{S,M_S},

$$\Psi(\boldsymbol{r},\boldsymbol{\sigma}) = \hat{\mathcal{A}} \left(\Xi_{S,M_S}(\boldsymbol{\sigma}) \sum_{l=1}^{K} c_l \, \psi_l(\boldsymbol{r}) \right). \tag{11}$$

The proper permutational symmetry of Ψ is ensured by applying the n-electron projector $\hat{\mathcal{A}}$. As the atomic basis functions $\psi_l(\boldsymbol{r})$ we employed exponentially correlated Gaussian (ECG) functions [24]

$$\psi_l(\boldsymbol{r}) = \exp\left[-\boldsymbol{r}^T \, \mathbf{A}_l \, \boldsymbol{r}\right] \tag{12}$$

and

$$\tilde{\boldsymbol{\psi}}_l(\boldsymbol{r}) = \boldsymbol{r}_i \exp\left[-\boldsymbol{r}^T \, \tilde{\mathbf{A}}_l \, \boldsymbol{r}\right] \tag{13}$$

of S and P symmetry, respectively. Each symmetric and positive definite matrix $\mathbf{A}_l$ contains $n(n+1)/2$ independent nonlinear parameters, so that the total trial wave function Ψ depends on a large number of the nonlinear parameters. This makes the function very flexible but at the same time difficult to optimize. To find optimal parameters of the wave function we evaluate the Rayleigh quotient

$$\varepsilon = \frac{\displaystyle\int \Psi^* \hat{H}_0 \, \Psi \, d\tau}{\displaystyle\int \Psi^* \Psi \, d\tau} \geq E_0 \tag{14}$$

which gives an upper bound to the exact energy. Through the trial function, ε also depends on a large number of linear and non-linear parameters with respect to which we want to find its minimum. During the minimization, ε has to be evaluated millions of times. From this point of view, it is very important that the evaluation of the matrix elements and the diagonalization of the Hamiltonian are efficiently programmed. Of course, finding the global minimum in such a large space is practically impossible and we have to be satisfied with some low-lying local minimum. The algorithm of the optimization we use is quite simple. In one step we optimize only the nonlinear parameters belonging to a single basis function while the rest is kept fixed. The optimal parameters found are frozen and, it the next step, we relax parameters of another basis function. Such an optimization on small subspaces is performed for all the basis functions, forming a cycle. We perform as many cycles as we find needed or feasible. The quality of the final results depends primarily on the effectiveness of the optimization, therefore much effort has been put into this time consuming part of the project.

IV. EXPECTATION VALUE IDENTITIES (EVI)

The matrix elements appearing in Section II can be relatively easily computed in the ECG basis. It is commonly known, however, that Gaussian-type bases poorly model the electron distribution nearby the interparticle coalescence points, which leads to a slow convergence of the singular operators expectation values. An elegant way to overcome this problem in the case of the Dirac delta has been suggested by Drachman [25]. He expressed the expectation value of $\delta(\boldsymbol{r}_{jk})$ by another expectation value containing less-singular operators

$$4\pi \left\langle \Psi \left| \delta(\boldsymbol{r}_{jk}) \right| \Psi \right\rangle = 2 \left\langle \Psi \left| \frac{1}{r_{jk}} (E - \hat{V}) \right| \Psi \right\rangle + \sum_i \left\langle \frac{1}{r_{jk}} \boldsymbol{\nabla}_i \Psi \right| \boldsymbol{\nabla}_i \Psi \right\rangle, \tag{15}$$

where $\hat{V}$ is the Coulomb potential energy operator. The same idea has been applied to the $\boldsymbol{\nabla}^4$ operator [26] leading to the following expectation value identity (EVI)

$$\left\langle \Psi \left| \boldsymbol{\nabla}_i^4 \right| \Psi \right\rangle = 4 \left\langle \Psi \left| (E - \hat{V})^2 \right| \Psi \right\rangle - 2 \sum_{i>j} \left\langle \boldsymbol{\nabla}_i^2 \Psi \right| \boldsymbol{\nabla}_j^2 \Psi \right\rangle, \tag{16}$$

and recently, a new EVI has been derived also for the Araki-Sucher term [27]

$$\left\langle \Psi \left| P\left(\frac{1}{r_{jk}^3}\right) \right| \Psi \right\rangle = 4\pi(1+\gamma)\left\langle \Psi \left| \delta(\boldsymbol{r}_{jk}) \right| \Psi \right\rangle + 2E \left\langle \Psi \left| \frac{\ln r_{jk}}{r_{jk}} \right| \Psi \right\rangle \tag{17}$$

$$- 2\left\langle \Psi \left| \frac{\ln r_{jk}}{r_{jk}} \hat{V} \right| \Psi \right\rangle + \sum_i \left\langle \frac{\ln r_{jk}}{r_{jk}} \boldsymbol{\nabla}_i \Psi \right| \boldsymbol{\nabla}_i \Psi \right\rangle .$$

The EVI's displayed above hold true only for the exact wave function. For the approximate wave functions the right hand side is supposed to converge faster than the conventional form. As we can see, the right hand side expressions look much more complicated than the original ones but fortunately we work in a Gaussian basis and, at least for atoms, the integrals, even these containing the logarithmic terms, can be written down in a closed form [27]. Convergence of the Breit operator in Eq. (4) is less problematic and its expectation values were computed conventionally.

V. THE BETHE LOGARITHM

The Bethe logarithm, $\ln k_0$, is a very slowly convergent quantity and its accurate evaluation is a difficult task. Until 2003, when two papers concerning lithium atom appeared [28, 29], precise values of $\ln k_0$ were known merely for one- and two-electron atoms and for one-electron molecular hydrogen cation [30]. In quantum chemical calculations involving the QED corrections for larger systems it is common to estimate $\ln k_0$ in a semiempirical way or even totally drop it. A justification for such treatment of the Bethe logarithm is its relatively small numerical contribution to the total α^3 correction as well as difficulties in its evaluation. In high precision calculations, however, $\ln k_0$ cannot be omitted. If we have in our disposal an accurate wave function we can compute $\ln k_0$ by means of the integral representation technique introduced by C. Schwartz [31] and developed by Korobov and Korobov [32] or by its more efficient modification introduced recently [29, 33]. In this new approach the Bethe logarithm of Eq. (7) is represented as a one-dimensional integral over the variable $t = 1/\sqrt{1+2\,\omega}$

$$\ln k_0 = \frac{1}{D} \int_0^1 \frac{f(t) - f_0 - f_2\, t^2}{t^3}\, dt, \tag{18}$$

where

$$f(t) = -\left\langle \Psi \left| \boldsymbol{\nabla} \frac{\omega}{H_0 - E_0 + \omega} \boldsymbol{\nabla} \right| \Psi \right\rangle , \tag{19}$$

and where ω is a frequency corresponding to the energy of a virtual photon. To evaluate (19), we need the first-order perturbation correction function, $\tilde{\mathbf{\Psi}}$, which is a solution to the first order perturbation equation with the perturbation defined by the nabla operator, Eq. (8). This operator couples the unperturbed S states with the intermediate states of P symmetry. This symmetry is reflected by the expansion of $\tilde{\mathbf{\Psi}}$ in the basis of the form (13). The nonlinear parameters defining this basis set were determined by minimizing the Hylleraas functional

$$\mathcal{J}_\omega\big[\tilde{\mathbf{\Psi}}\big] = \langle\tilde{\mathbf{\Psi}}\big|H_0 - E_0 + \omega\big|\tilde{\mathbf{\Psi}}\rangle + 2\langle\tilde{\mathbf{\Psi}}\big|\mathbf{\nabla}\big|\Psi\rangle \tag{20}$$

at several different values of ω. For the precision of the final result it is crucial that $f(t)$ is computed to a high accuracy. Therefore, much effort has been put into the optimization of the first order correction function $\tilde{\mathbf{\Psi}}$ entering the functional (20).

An important factor deciding on the accuracy of $\ln k_0$ is the treatment of the small t asymptotics of the integrand in Eq. (18). As shown by C. Schwartz [31], at very low values of t, the integrand can be represented as

$$f(t) = f_0 + f_2\, t^2 + f_3\, t^3 + f_4\, t^4\, \ln(t) + o(t^4)\,, \tag{21}$$

where the lowest order coefficients are known to be $f_0 = -\langle\Psi\,|\mathbf{\nabla}^2|\,\Psi\rangle$, $f_2 = -2\,D$, $f_3 = 8\,Z\,D$, and $f_4 = 16\,Z^2\,D$, and where the higher order coefficients are determined by fitting to $f(t)$ of Eq. (19).

VI. RESULTS AND DISCUSSION

The wave function for Li^- has been obtained in the spirit of the method described in Ref. [34]. Three different basis sets built of 2400, 1200, and 600 basis functions have been optimized with respect to the energy of three subsequent states of Li^-: 2^1S, 3^1S, and 4^1S, respectively. These three bases were then merged together forming the final 4200-term basis for the wave function. In a similar way the wave function for the Lithium atom has been built. Three bases of the size 2400, 2000, and 800, optimized against the 2^2S, 3^2S, and 4^2S energies of Li have been glued together to obtain a 5200-term basis for diagonalization of the Lithium Hamiltonian. Note that, thanks to the variational principle, the resultant basis always leads to the energies lower than (or at worse equal to) the corresponding energies obtained from its particular components. The main challenge in this project is the construction of the accurate nonrelativistic wave function, Ψ, for the four-electron Lithium anion. An obvious, though not the only, measure of the quality of the wave function is the energy, E_0. The nonrelativistic clamped nuclei energy $E_0 = \langle H_0 \rangle$ of Li^- reported here is the lowest upper bound available to date. It is about 4 μE_h lower than the best previous variational energy for this anion [35] and we estimate that it lies ca. 0.8 μE_h above the exact energy. The corresponding ECG energy of the Lithium atom is by 3.4 nE_h higher than the most accurate to date result obtained in Ref. [15]. The nonrelativistic wave functions obtained this way for the ground states of Li^- and Li were subsequently employed to compute the expectation values of several operators appearing in the expressions (2)-(10). In the case of the singular operators, namely $\delta(\boldsymbol{r})$, p^4, and $P(1/r^3)$ their expectation values were computed using more regular expressions resulting from the EVI's of Eqs. (15)-(17). Numerical values of all the expectation values needed to evaluate the components the α-expansion (1) are listed in Table I.

As mentioned in Section V, the precise evaluation of the Bethe logarithm requires the $f(t)$ function of Eq. (19) to be accurately determined in a possibly wide range of their arguments and using $\tilde{\boldsymbol{\Psi}}$ optimized just for the static case ($\omega = 0$) is insufficient. For this reason, the basis for $\tilde{\boldsymbol{\Psi}}$ has been assembled in the way similar to that described for Ψ above. Four different 1200-term bases have been optimized using functional (20) at four different frequencies $\omega = 0, 10, 100$, and 200. When combined together, they formed a final 4800-term basis of $\tilde{\boldsymbol{\Psi}}$ employed farther to evaluate $f(t)$ at any t needed.

The methodology described in this and in the previous sections was employed to determine theoretically the electron affinity of the Lithium atom. The components of the α-expansion (1) and the final energy levels of the ground state of Li^- and Li are presented in Table II. Accurate calculation of EA as a difference of two comparatively large numbers can be accomplished if both the components are determined with a high degree of precision. In this work, all the corrections to the nonrelativistic energy are computed to an accuracy significantly exceeding that which has been reached for E_0. The uncertainty in the relativistic correction (0.005 cm^{-1}), contributes minimally to the final uncertainty of EA and the latter is practically determined by the error of the nonrelativistic contribution. The uncertainty of the relativistic correction comes mainly from the kinetic energy term (0.003 cm^{-1}). The nuclear Dirac delta and the orbit-orbit terms contribute 0.001 cm^{-1}

each, and the electron-electron Dirac delta's uncertainty is neglegible. As the error made in our three-electron calculations is approximately two orders of magnitude smaller than that in the four-electron calculations, we conclude that the decisive source of the uncertainty lies in the error of the E_0 value for Li^-. In order to further diminish the theoretical uncertainty, the accuracy of this quantity must be increased. Currently, however, apart from the ECG method no other method offers higher accuracy for the four-electron systems. We expect, though, that the Hylleraas approach might be a good candidate to bring progress in this field.

It can be inferred from Table II that, to a large degree, the relativistic and QED correction for the Lithium ion and atom cancel out, so that their overall contribution to the EA is relatively small. In fact this contribution is close to the final uncertainty on EA. This supports opinions on the decisive role played by electron correlation in the binding of the outermost electron. Our target quantity, the EA of Lithium, amounts to ca. $23\,mE_h$ which is of the same order as the correlation energy in Li^- ($73\,mE_h$) and in Li ($45\,mE_h$). Interestingly, calculations at the Hartree-Fock level of theory yield the EA equal to $-0.45\,mE_h$ [36] which leads to the unphysical conclusion that Li^- is unstable. The importance of the electron correlation is in general more exposed in negative ions than in the other members of their isoelectronic series because, relative to the interelectron interaction, the electron-nucleus interaction is the weakest. The high expectations concerning the description of the electron correlation imposed on the trial function are met by the ECG wave function which allowed us to obtain accurate results.

The stable Lithium negative ion was first observed by Ya'akobi in 1966 [37]. He also gave the first estimate of 0.6 eV $= 4.8{\cdot}10^3$ cm^{-1} for the Lithium EA. A few years later, Scheer and Fine inferred from their experiment that the EA should be greater than $5.2{\cdot}10^3$ and less than $8.5{\cdot}10^3$ cm^{-1} [38]. This apparent discrepancy was the driving force for a variety of experimental studies—the most recent of them are listed in the bottom part of Table II. The most accurate value of EA of Li was determined by Haeffler and coworkers in 1996 [39]. Their result is in excellent agreement with our outcome. A graphical comparison of the selected experimental data and the theoretical result obtained in this work is presented in Figure 1.

There have also been a large number of theoretical studies of EA of Li. References to many older works can be found in [38, 40–43]. Among the latest works one should mention the contributions by Chung and Fullbright [44], Fisher [45], and Gdanitz [46]. While the older theoretical results are spread over more than 5000 cm^{-1}, in most cases underestimating the experimental value, the most recent studies predicted EA to an accuracy of a few cm^{-1}. In the present work we decreased the difference between the theory and the most precise measurements to a small fraction of the wavenumber so that as much as five significant digits of these two numbers tally.

VII. CONCLUSIONS

The ECG method in connection with the α-expansion method is able to provide high accuracy results for light atoms composed of a few electrons [33, 48]. The ECG wave function enables the electron correlation to be included in practically 100 %, whereas the α-expansion of the energy, together with the effective methods of computing its singular components, provides a correct description of all the essential physical effects. Further development of this methodology might go in two directions: improvement in the quality of the nonrelativistic wave function and search for better optimization methods, which would allow consideration of larger systems.

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[1] P. J. Mohr and B. N. Taylor, Rev. Mod. Phys. **77**, 1 (2005).

[2] V. A. Yerokhin, P. Indelicato, and V. M. Shabaev, Phys. Rev. A **71**, R040101 (2005).

[3] D. C. Morton, Q. Wu, and G. W. F. Drake, Can. J. Phys. **84**, 83 (2006).

[4] K. Pachucki, Phys. Rev. Lett. **84**, 4561 (2000).

[5] V. Korobov and A. Yelkhovsky, Phys. Rev. Lett. **87**, 193003 (2001).

[6] A. Czarnecki, U. Jentschura, and K. Pachucki, Phys. Rev. Lett. **95**, 180404 (2005).

[7] A. Huber, Th. Udem, B. Gross, J. Reichert, M. Kourogi, K. Pachucki, M. Weitz, and T. W. Hänsch, Phys. Rev. Lett. **80**, 468 (1998).

[8] R. Sanchez et al., Phys. Rev. Lett. **96**, 033002 (2006).

[9] M. Puchalski, A. M. Moro, and K. Pachucki, Phys. Rev. Lett. **97**, 133001 (2006).

[10] C. Schwartz, arXiv:physics/0208004 (2002).

[11] W. Cencek and J. Rychlewski, quoted in [16] on p. 110.

[12] Y. Kurokawa, H. Nakashima, and H. Nakatsuji, Phys. Rev. A **72**, 062502 (2005).

[13] J. S. Sims and S. A. Hagstrom, J. Chem. Phys. **124**, 094101 (2006).

[14] Z.-C. Yan and G. W. F. Drake, Phys. Rev. A **52**, 3711 (1995).

[15] M. Puchalski and K. Pachucki, Phys. Rev. A **73**, 022503 (2006).

[16] J. Rychlewski and J. Komasa, *Explicitly correlated functions in variational calculations* in: J. Rychlewski (Ed.) *Explicitly Correlated Wave Functions in Chemistry and Physics* (Kluwer Academic Publishers, Dordrecht, 2003), p. 91.

[17] K. Pachucki, J. Phys. B **31**, 3547 (1998).

[18] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics Of One- And Two-Electron Atoms*, (Plenum Publishing Corporation, New York, 1957).

[19] H. Araki, Prog. Theor. Phys. **17**, 619 (1957).

[20] J. Sucher, Phys. Rev. **109**, 1010 (1958).

[21] K. Pachucki, Phys. Rev. A **71**, 012503 (2005).

[22] K. Pachucki, Phys. Rev. A **74**, 022512 (2006).

[23] A. Beckmann, K. D. Bökklen, and D. Elke, Z. Phys. **270**, 173 (1974).

[24] K. Singer, Proc. R. Soc. London, Ser. A **258**, 412 (1960).

[25] R. J. Drachman, J. Phys. B **14**, 2733 (1981).

[26] G. W. F. Drake, in *Long-Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*, edited by F. S. Levine and D. A. Micha (Plenum Press, New York, 1993), p. 107.

[27] K. Pachucki, W. Cencek, and J. Komasa, J. Chem. Phys. **122**, 184101 (2005).

[28] Z.-C. Yan and G.W.F. Drake, Phys. Rev. Lett. **91**, 113004 (2003).

[29] K. Pachucki and J. Komasa, Phys. Rev. A **68**, 042507 (2003).

[30] R. Bukowski, B. Jeziorski, R. Moszynski, and W. Kołos, Int. J. Quantum Chem. **42**, 287 (1992).

[31] C. Schwartz, Phys. Rev. **123**, 1700 (1961).

[32] V. I. Korobov and S. V. Korobov, Phys. Rev. A **59**, 3394 (1999).

[33] K. Pachucki and J. Komasa, Phys. Rev. Lett. **92**, 213001 (2004).

[34] J. Komasa, Phys. Rev. A **65**, 012506 (2002).

[35] J. Komasa, J. Rychlewski, and K. Jankowski, Phys. Rev. A **65**, 042507 (2002).

[36] J. S. Sims, S. A. Hagstrom, D. Munch, and C. F. Bunge, Phys. Rev. A **13**, 560 (1976).

[37] B. Ya'akobi, Phys. Lett. **23**, 655 (1966).

[38] M. D. Scheer and J. Fine, J. Chem. Phys. **50**, 4343 (1969).

[39] G. Haeffler, D. Hanstrop, I. Kiyan, A. E. Klinkmüller, and U. Ljungblad, Phys. Rev. A **53**, 4127 (1996).

[40] Y. K. Bae and J. R. Peterson, Phys. Rev. A **32**, 1917 (1985).

[41] A. Kasdan and W. C. Lineberger, Phys. Rev. A **10**, 1658 (1974).

[42] R. L. Graham, D. L. Yeager, and A. Rizzo, J. Chem. Phys. **91**, 5451 (1989).

[43] J. Dellwo, Y. Liu, D. J. Pegg, and G. D. Alton, Phys. Rev. A **45**, 1544 (1992).

[44] K. T. Chung and P. Fullbright, Phys. Scr. **45**, 445 (1992).

[45] C. F. Fisher, J. Phys. B **26**, 855 (1993).

[46] R. Gdanitz, J. Chem. Phys. **110**, 706 (1999).

[47] D. Feldmann, Z. Phys. A **277**, 19 (1976).

[48] K. Pachucki and J. Komasa, Phys. Rev. A **73**, 052502 (2006).

TABLE I: Expectation values (in atomic units) of various operators with nonrelativistic wave functions of Li^- (K=4200) and Li (K=5200).

	Li^-	Li
$\langle\Psi\,\lvert H_0\rvert\,\Psi\rangle$	$-7.500\,776\,4(8)$	$-7.478\,060\,320(4)$
$\left\langle\Psi\,\left\lvert\boldsymbol{\nabla}^2\right\rvert\,\Psi\right\rangle$	$-15.617\,761(8)$	$-15.559\,806\,2(1)$
$\langle\Psi\,\lvert\delta(\boldsymbol{r}_i)\rvert\,\Psi\rangle$	$13.838\,08(20)$	$13.842\,606(4)$
$\langle\Psi\,\lvert\delta(\boldsymbol{r}_{ij})\rvert\,\Psi\rangle$	$0.544\,214\,2(6)$	$0.544\,324\,4(3)$
$\langle\Psi\,\lvert\boldsymbol{p}_i\cdot\boldsymbol{p}_j\rvert\,\Psi\rangle$	$0.308\,104(3)$	$0.301\,842\,78(1)$
$\left\langle\Psi\,\left\lvert p_i^4\right\rvert\,\Psi\right\rangle$	$628.203(2)$	$628.453\,1(50)$
$\langle\Psi\lvert r_{ij}^{-3}\,\boldsymbol{r}_{ij}\,(\boldsymbol{r}_{ij}\cdot\boldsymbol{p}_i)\,\boldsymbol{p}_j+$		
$r_{ij}^{-1}\boldsymbol{p}_i\cdot\boldsymbol{p}_j\lvert\Psi\rangle/2$	$-0.431\,345(60)$	$-0.435\,599(25)$
$\left\langle\Psi\,\left\lvert P(1/r_{ij}^3)\right\rvert\,\Psi\right\rangle/4\pi$	$-0.024\,235(14)$	$-0.021\,768(12)$
$\ln k_0$	$5.177\,78(5)$	$5.178\,17(3)$

TABLE II: Electron affinity (EA) of Lithium

	Li^-/E_h	Li/E_h	$\mathrm{EA}/\mathrm{cm}^{-1}$
E_0	$-7.500\,776\,444$	$-7.478\,060\,320$	4985.61(18)
E_{FM}	$0.000\,610\,791$	$0.000\,608\,525$	$-0.497(0)$
$\alpha^2 E_{\mathrm{REL}}$	$-0.000\,640\,967$	$-0.000\,641\,703$	$-0.161(5)$
$\alpha^3 E_{\mathrm{QED}}$	$0.000\,111\,339$	$0.000\,111\,361$	0.007(0)
$\alpha^4 E_{\mathrm{HQED}}$	$0.000\,003\,397$	$0.000\,003\,398$	0.000(0)
E	$-7.500\,691\,884$	$-7.477\,978\,739$	4984.96(18)
Experiment:	Haeffler et al., 1996, [39]		4984.90(17)
	Dellwo et al., 1992, [43]		4981.3(16)
	Bae and Peterson, 1985, [40]		4978.9(56)
	Feldmann, 1976, [47]		4986.1(40)

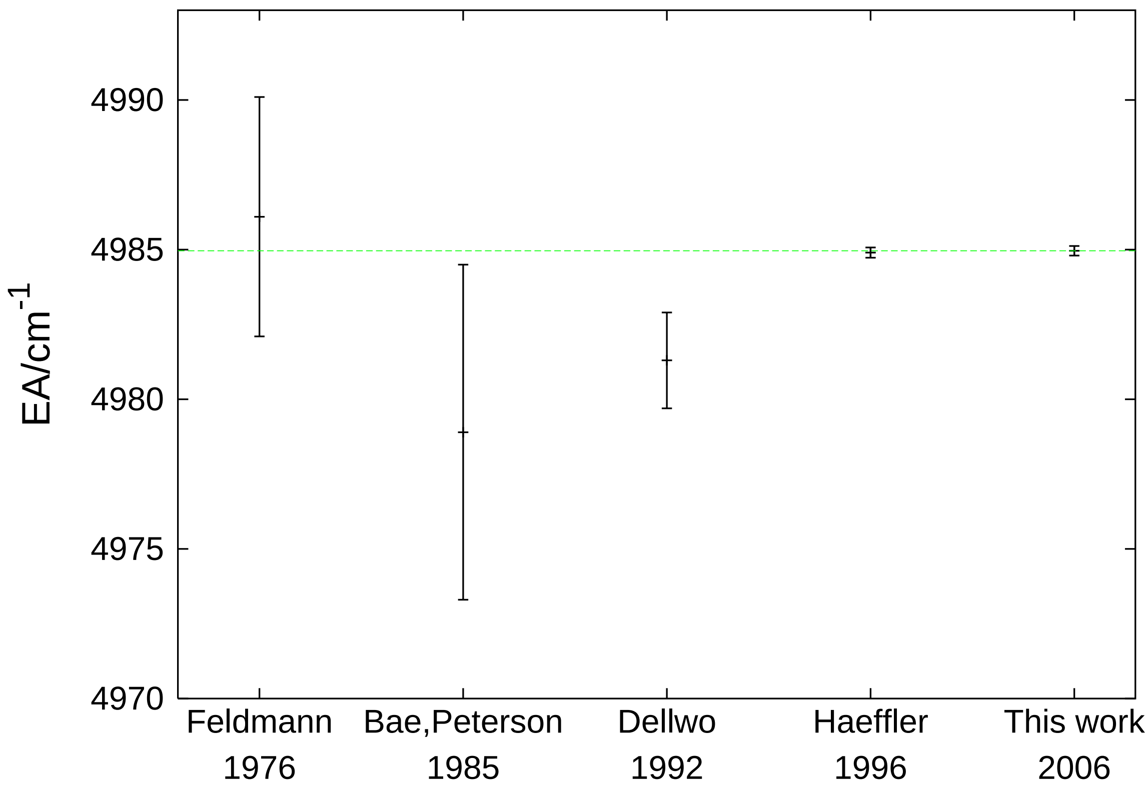

FIG. 1: Electron affinity (EA) of the Lithium atom. A comparison of the various experimental data with the EA predicted in this work by the ECG method.

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