An accurate few-parameter ground state wave function for the Lithium atom

Nicolais L. Guevara[*] and Frank E. Harris[†]
Quantum Theory Project, Departments of Physics and Chemistry,
University of Florida, Gainesville, FL 32611-8435, USA

Alexander V. Turbiner[‡]
Institut des Hautes Études Scientifiques,
Bures-sur-Yvette, F-91440, France,
and
Instituto de Ciencias Nucleares,
Universidad Nacional Autónoma de México,
Apartado Postal 70-543,
04510 México, D.F., México

Abstract

A simple, seven-parameter trial function is proposed for a description of the ground state of the Lithium atom. It includes both spin functions. Inter-electronic distances appear in exponential form as well as in a pre-exponential factor, and the necessary energy matrix elements are evaluated by numerical integration in the space of the relative coordinates. Encouragingly accurate values of the energy and the cusp parameters as well as for some expectation values are obtained.

---

[*] Electronic address: `guevara@qtp.ufl.edu`
[†] Electronic address: `harris@qtp.ufl.edu`
[‡] Electronic address: `turbiner@nucleares.unam.mx`

I. INTRODUCTION

It is well-known that the standard quantum chemistry approaches to calculation of the energies of the low-lying states of few-electron atoms are characterized by slow convergence. This convergence problem was demonstrated in a discouragingly explicit way for the case of the Helium atom in recent studies by Korobov [1] (using a sort of exponential Hylleraas basis) and by Schwartz [2] (using various trial functions that included correlated exponentials, pre-exponential integer and fractional powers of both nuclear-electron and electron-electron distances, as well as logarithmic terms). An unpleasant drawback of these studies is an absence of confidence that high accuracy obtained for the energy guarantees a comparable accuracy in expectation values [18] This question is vital when relativistic corrections are studied, particularly in view of the fact that some of these corrections are defined by the expectation values of singular and/or local quantities (for a discussion see e.g. [3]). Recent advances in experimental techniques have now led to experimental data whose understanding requires an accurate knowledge of the relativistic corrections [5]. As one of possible ways to handle this situation, one of the present authors (FEH) has proposed to look for simple, few-parameter "ultra-compact" trial functions which guarantee reasonably high overall accuracy. One way of characterizing this approach is to describe it as a search for the most accurate few-parameter trial functions. This line of endeavor is illustrated by work on the H_2 molecule [6], for which a nearly optimum 14-parameter function was reported, and by work on the He isoelectronic series [7], where optimum wavefunctions of up to four configurations were generated.

The present contribution deals with a search for an optimum ultra-compact wavefunction for the ground state of the Li atom. An important issue for such a study is how to determine the overall quality of a trial function. The viewpoint taken in the present work is to use as a quality measure the error in the cusp parameters obtained from the trial function (residues arising from the Coulomb singularities of the potential). Of course, this criterion becomes reasonable only if the cusp conditions are not artificially fixed to their exact values by the choice of form for the trial function. We note that the most popular methods for atomic computations use Gaussian-type orbitals, and that while such bases can provide extremely accurate energies, they usually lead to vanishing cusp parameters and thereby have significant drawbacks for the description of relativistic and other local effects.

In the work reported here, the trial functions that were examined consist of exponentials in all the relative coordinates, in some cases multiplied by pre-exponential factors dependent linearly on the interparticle distances. The matrix elements that arise have been evaluated numerically by methods used previously by one of the authors [8].

II. WAVEFUNCTION AND VARIATIONAL METHOD

The nonrelativistic Hamiltonian for the Lithium atom under the Born-Oppenheimer approximation of zero order, i.e. with the Li nucleus assumed to be of infinite mass, is (in Hartree atomic units)

$$\mathcal{H} \;= -\sum_{i=1}^{3}\left(\frac{1}{2}\nabla_i^2 \;+\; \frac{Z}{r_i}\right) \;+\; \sum_{i=1}^{3}\sum_{j>i}^{3} \frac{1}{r_{ij}} \ , \tag{1}$$

where ∇_i is the 3-vector of the momentum of the ith electron, Z is the nuclear charge (here Z=3), r_i is the distance between the ith electron and the Li nucleus, and r_{ij} are the interelectron distances. The kinetic energy part of $\mathcal{H}$ is conveniently written in terms of the distance coordinates r_i and $u_k = r_{ij}, k \neq i \neq j$ [9, 10],

$$\begin{aligned}\sum_{i=1}^{3} {\nabla_i}^2 \;&=\; \sum_{i=1}^{3}\left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i} + 2\frac{\partial^2}{\partial u_i^2} + \frac{4}{u_i}\frac{\partial}{\partial u_i}\right) \\ &+\; \sum_{P}\left(\frac{r_i^2+u_k^2-r_j^2}{u_k r_i}\,\frac{\partial^2}{\partial r_i \partial u_k} + \frac{1}{2}\,\frac{u_i^2+u_k^2-u_j^2}{u_i u_k}\,\frac{\partial^2}{\partial u_i \partial u_k}\right) ,\end{aligned} \tag{2}$$

as long as the wave function has no explicit angular dependence. The summation P runs over i, j, k which are the six permutations of $1, 2, 3$.

The variational method is used to study the ground state of the Lithium atom. Physical relevance arguments are followed to choose the trial function (see, e.g. Turbiner [11]). In particular, we construct wavefunctions which allow us to reproduce both the Coulomb singularities in r_i and in r_{ij} and the correct asymptotic behavior of large distances. As a result the wavefunction of the $^2S_{1/2}$ Li ground state is written in the particular form

$$\psi = \mathsf{A}\left[\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3)\chi\right] \ , \tag{3}$$

with

$$\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3) = f(r_1,r_2,r_3,r_{12},r_{13},r_{23})e^{-\alpha_1 r_1-\alpha_2 r_2-\alpha_3 r_3-\alpha_{12} r_{12}-\alpha_{13} r_{13}-\alpha_{23} r_{23}} \ , \tag{4}$$

where the pre-exponential factor is a linear function of its arguments, while α_i and α_{ij} are (non-linear) parameters. A is the three-particle *antisymmetrizer*

$$\mathsf{A} = I - P_{12} - P_{13} - P_{23} + P_{231} + P_{312} \ . \tag{5}$$

Here P_{ij} represents the permutation $i \leftrightarrow j$ and P_{ijk} stands for the permutation of 123 into ijk. In Eq. (3), χ denotes a doublet spin eigenfunction ($S = 1/2$) expressed as a linear combination

$$\chi \ = \ \chi_1 + B\chi_2 \tag{6}$$

of two linearly independent spin functions spanning the doublet spin space of quantum numbers $S = 1/2$, $M_s = 1/2$:

$$\chi_1 = 2^{-1/2}\ [\alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3)], \tag{7}$$

and

$$\chi_2 = 6^{-1/2}\ [2\alpha(1)\alpha(2)\beta(3) - \beta(1)\alpha(2)\alpha(3) - \alpha(1)\beta(2)\alpha(3)]. \tag{8}$$

In Eq. (6), B is a parameter which can be used to obtain the optimum spin function, and $\alpha(i), \beta(i)$ are spin up, down functions of electron i. In total, the function ψ of Eq. (3) is characterized by seven parameters, plus any that may occur in the pre-exponential factor f.

The matrix elements of $\mathcal{H}$ can be written as integrals over the nine dimensions represented by $\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$. Integrations over three dimensions describing overall orientation are easily performed, and we end up with six-dimensional integrals over the relative coordinates $(r_1, r_2, r_3, r_{12}, r_{13}, r_{23})$. While it is in principle possible to reduce these integrals analytically to one-dimensional integration: to expressions involving dilogarithm functions, as first shown by Fromm and Hill [12], the analytic properties of the resulting expressions were found to be quite complicated (see Harris [13]). For that reason, the primary method used in the present research was direct six-dimensional numerical integration.

These numerical integrations were carried out using a suitable partitioning of the $\mathbf{R^6}$ to subdomains based on a profile of the integrand (for details, see e.g. Turbiner and Lopez [8]). In each subdomain the numerical integration is done with a relative accuracy of $\sim 10^{-5}$ to 10^{-6} by use of the adaptive D01FCF routine from NAG-LIB [14] in a parallel manner. Due to the complicated profiles of the integrands the numerical calculations are very difficult and if not done with great care can lead to a serious loss of accuracy. By comparing numerical and analytical evaluations of some of the simpler matrix elements, it was verified that the numerical methods were reliable at least to six significant digits.

Minimization of the energy with respect to the nonlinear parameters was performed using the minimization package MINUIT from CERN-LIB [15].

III. RESULTS

The Li ground-state energies obtained for optimized variational wavefunctions of the form given in Eqs. (3) and (4) are displayed in Table I; the corresponding optimized variational parameters are given in Table II. Each of the first seven rows of Table I describes a wavefunction with a different pre-exponential factor; the last row of the table reports the energy obtained from the most accurate existent Li ground-state calculation [3], a result extrapolated from a 9576-term wavefunction of Hylleraas type and probably accurate to within 10^{-9} a.u. Using these wave functions we calculated the variational energies and also the values of the cusp parameters:

$$C = \frac{\langle\psi|\,\delta(\vec{r})\frac{\partial}{\partial r}|\psi\rangle}{\langle\psi|\,\delta(\vec{r})|\psi\rangle} \ , \tag{9}$$

[cf. [16], Eq. (18)], which for the exact wavefunction should be equal to -3 when $\vec{r} = \vec{r}_i$ (the electron-nuclear cusp).

All the wavefunctions described in Table II display the expected electronic shell structure; electrons 1 and 2 correspond to a $1s^2$ pair, with an average exponential parameter that exhibits only a small degree of screening relative to the bare-nucleus value $\alpha = 3$. Significant energy improvement has been achieved by the "split-shell" description of this electron pair (with $\alpha_1 > 3 > \alpha_2$). Electron 3 (to zero order the $2s$ electron) is not optimally described by a pure exponential, and great improvement is obtained by giving it a Slater-type orbital (STO) description, as in ψ_2, or even a hydrogenic $2s$ form, as in ψ_4. Note that the sign of the pre-factor parameter β_1 produces the node characteristic for a $2s$ orbital. The data for ψ_3 and ψ_5 show that inclusion of a linear interelectron distance improves the variational energy (as indeed it must), but the improvement is not as striking as that associated with the factor r_3. Incidentally, most of the improvement associated with the insertion of the factor r_{13} in ψ_3 simply reflects the fact that with high probability, r_{13} is similar in magnitude to r_3. This observation becomes evident when one notes that the r_1 distribution is $1s$-like and far more localized than is the $2s$-like r_3 distribution. Further flexibility, as in ψ_6 (the best three-term

TABLE I: Li ground-state energy E, cusp parameter C_{eN} [see Eq. (9)] and the expectation values $\langle r_{ij}^{-1}\rangle, \langle r_{ij}\rangle$ for the trial function in Eq. (3) with various pre-factors f.

	$f(r_1, r_2, r_3, r_{12}, r_{13}, r_{23})$	E (a.u.)	$-C_{eN}$	$\langle r_{ij}^{-1}\rangle$	$\langle r_{ij}\rangle$
ψ_1	1	-7.4547	2.953	2.1732	10.0046
ψ_2	r_3	-7.4712	2.958	2.1965	8.9553
ψ_3	r_{13}	-7.4682	2.955	2.1922	8.9457
ψ_4	$(1+\beta_1\ r_3)$ [a]	-7.4727	2.958	2.2091	8.6552
ψ_5	$(1+\gamma_1\ r_{13})$ [b]	-7.4686	2.955	2.1990	8.8953
ψ_6^*	$(1+\beta_1\ r_3+\gamma_1\ r_{13})$ [c]	-7.4451	2.901	2.2501	8.7688
ψ_6	$(1+\beta_1\ r_3+\gamma_1\ r_{13})$ [d]	-7.4729	2.961	2.2027	8.7330
'Exact'		-7.47806[e]	3.0	2.1982[f]	8.6684[f]

[a] $\beta_1 = -2.44486$

[b] $\gamma_1 = 9.53316$

[c] $\beta_1 = -3.82716,\ \gamma_1 = -0.47333$

[d] $\beta_1 = -2.77713,\ \gamma_1 = -0.26645$

[e] from Ref. [3] (rounded)

[f] from Ref. [4] (rounded).

prefactor) gives little additional gain over that already achieved in ψ_4. All the wavefunctions also exhibit small negative values of the interelectron screening parameters α_{ij}, thereby improving the description of the repulsive electron-electron correlation. However, neglecting this screening by setting all $\alpha_{ij} = 0$ (see the function ψ_6^*, Table II) worsens significantly the variational energy as well as the cusp parameter, see Table I. Note that a function of this type was used in [3], yielding the most accurate variational energy thus far obtained, but at the expense of a very long expansion.

All the results reported in this paper use the doublet spin function that optimizes the trial energy for the given spatial function. From the small values of B in Table II, we see that in every case the dominant contributor to the spin state is (as expected) that which couples the $1s$ and $1s'$ spatial functions into a spin singlet. However, inclusion of the other member of the spin basis does influence the energy to some extent; for ψ_1 (the trial function

TABLE II: Variational parameters α_i and α_{ij} in [a.u.]$^{-1}$ and B (dimensionless) for some trial functions from Table I.

	ψ_1	ψ_2	ψ_4	ψ_6^*	ψ_6
α_1	3.2892	3.3065	3.3038	3.3051	3.3044
α_2	2.3343	2.3291	2.3519	2.0657	2.3603
α_3	0.4336	0.7004	0.7473	0.6690	0.7327
α_{12}	−0.2108	−0.2050	−0.2150	0.	−0.2218
α_{13}	−0.0411	−0.0311	−0.0194	0.	−0.0227
α_{23}	−0.0404	−0.0316	−0.0313	0.	−0.0276
B	0.06295	0.01416	−0.00201	0.00277	−0.00202

with the largest optimum B), use of the second spin state lowers the trial energy by about 0.001 a.u.

Recently, it was shown by one of the authors [17] that a correct treatment of the domain of WKB asymptotics of the wavefunction at large distances is very important for getting a high quality trial function. Usually, the large-distance asymptotic expansion of the exponential phase of the wavefunction contains several terms that grow as the distance increases. All these terms should be reproduced in a trial function, otherwise exponential deviation from the exact function at large distances occurs. In the case of Lithium it can be verified that

$$\varphi \equiv -\log\psi = a_1 r_3 + a_2 \log r_3 + \mathrm{O}(1)\ , \quad r_3 \to \infty\ ,\ r_{1,2}\ \text{fixed}\ , \tag{10}$$

where $a_{1,2}$ are constants. These two terms in the expansion are the only terms that grow as r_3 increases, and failure to reproduce them in the trial function can lead to an exponentially large deviation of the trial function from the exact eigenfunction at large (and intermediate) distances r_3. All six of the functions we study reproduce at least the linear term in Eq. (10) and all but ψ_1 reproduce both terms. This observation might be considered as an explanation why ψ_1 gives worse results for energy than the other wavefunctions (see Table I). Unfortunately, at this time a complete analysis of the asymptotic behavior of the exponential phase at large distances (in different directions in 6D r-space) is missing; such an analysis would be helpful for the identification of adequate trial functions.

Following the above analysis, it is not surprising that the function ψ_1 gives the largest deviation from the exact values in both the energy ($\sim 0.5\%$) and the cusp parameter C_{eN} ($\sim 1.6\%$), while for the most accurate function ψ_6 these deviations are respectively $\sim 0.01\%$ and $\sim 1.3\%$. It is worth noting that for the functions ψ_{1-6} an increase of the accuracy in energy corresponds to a decrease of the error in the cusp parameter C_{eN} (see Table I). A similar situation occurs for the expectation value $\langle r_{ij}\rangle$ in comparison with the value reported in [4]. For $\langle r_{ij}^{-1}\rangle$ the largest deviation from the result from [4] occurs for the function ψ_1 which also provides the largest deviation for energy, cusp parameter and $\langle r_{ij}\rangle$. We must emphasize that all deviations in energy as well as in the expectation values occur systematically at the third significant digit.

IV. CONCLUSION

Simple and compact few-parameter trial functions are presented for the ground state of the Lithium atom. These already provide a very accurate ground state energy. These functions ψ_{1-6} are the most accurate among existent few-parameter trial functions. However, the presented analysis does not seem final since one could explore the more extended prefactor

$$f(r_1, r_2, r_3, r_{12}, r_{13}, r_{23}) = (1 + \beta_1\ r_1 + \beta_2\ r_2 + \beta_3\ r_3 + \gamma_1\ r_{23} + \gamma_2\ r_{13} + \gamma_3\ r_{12})\ ,$$

which seems beyond the computer resources presently available to us.

The wavefunctions used in the present work can be easily modified to study excited states of the Lithium atom.

Acknowledgments

Two of the present authors (NLG and AVT) dedicate this work to the third author (FEH) on the occasion of his 80th birthday.

NLG and AVT express their deep gratitude to J.C. López Vieyra (ICN-UNAM) for his interest in the work and for numerous useful discussions. NLG thanks the Instituto de Ciencias Nucleares (UNAM, Mexico City) and AVT thanks the Physics Department (UF, Gainesville) for the warm hospitality where a part of the present work was done. AVT thanks

IHES (Bures-sur-Yvette, France) for the hospitality extended to him where the present work was completed. FEH acknowledges support of the U.S. National Science Foundation, Grant PHY-0601758. The work of AVT was partially supported by DGAPA **IN121106-3** and CONACyT **47899-E, 58942-F** grants. Actual computations were done on a 54-node FENOMEC cluster ABACO (IIMAS) at UNAM in México City.

[1] V. I. Korobov, *Phys. Rev. A* **66**, 024501 (2002).

[2] C. Schwartz, *Int. J. Mod. Phys. E* **15**, 877 (2006).

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

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

[5] M. I. Eides, H. Grotch, and V. A. Shelyuto, 'Theory of Light Hydrogenic Bound States', Springer Tracts in Modern Physics , Vol. 222 (2007) 262 p. ISBN: 978-3-540-45269-0

[6] A.V. Turbiner and N.L. Guevara, *Collect. Czech. Chem. Commun.* **72**, 164 (2007).

[7] F.E. Harris and V.H. Smith, Jr., *Adv. Quantum Chem.* **48**, 407 (2005).

[8] A.V. Turbiner and J.C. López Vieyra, *Phys. Repts.* **424**, 309 (2006).

[9] S. Larsson, *Phys. Rev.* **169**, 49 (1968).

[10] F.W. King, *J. Mol. Struct. (Theochem)* **400**, 7 (1997).

[11] A.V. Turbiner, *Usp. Fiz. Nauk.* **144**, 35 (1984) [*Sov. Phys. Usp.* **27**, 668 (1984)].

[12] D.M. Fromm and R.N. Hill, *Phys. Rev. A* **36**, 1013 (1987).

[13] F.E. Harris, *Phys. Rev. A* **55**, 1820 (1997).

[14] NAG Fortran Library Mark 19.

[15] CERN Program Library Long Writeup D506. MINUIT. *Function Minimization and Error Analysis* Reference Manual, Version 94.1, F. James, CERN Geneva, Switzerland (1994-1998).

[16] K. Pachucki and J. Komasa, *Chemical Physics Letters* **389**, 209 (2004).

[17] A.V. Turbiner, *Letters in Mathematical Physics* **74**, 169-180 (2005).

[18] It is worth emphasizing that in the literature there sometimes appear misleading statements about accurate wavefunctions without any explanation of the meaning of the word "accurate"; as pointed out in [3] the only accuracy measure usually identified is the energy. Moreover, there are explicit examples in which a straightforward extrapolation of the variational energy (and expectation values) to the exact energy leads to inaccurate results (see e.g. discussion in [4]).