# High-accuracy calculations of the lowest eleven Rydberg ${ }^{2}$ P states of the Li atom 

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#### Abstract

Highly accurate calculations are reported for the eleven lowest states of the ${ }^{2} P$ Rydberg series $\left(1 s^{2} n p^{1}, n=2, \ldots, 12\right)$ of the lithium atom. The nonrelativistic wave functions of the states are expanded in terms of up to 16000 all-electron explicitly correlated Gaussian (ECG) basis functions. The ECG exponential parameters are variationally optimized using a method that employs the analytical energy gradient determined for the parameters. The finite-nuclear-mass effects of the ${ }^{6} \mathrm{Li}$ and ${ }^{7} \mathrm{Li}$ isotopes are explicitly included in the nonrelativistic variational calculations. The results also include the leading relativistic and quantum electrodynamics energy corrections computed using the framework of perturbation theory. The calculated interstate transition energies are compared with the available experimental data. The ${ }^{6} \mathrm{Li}^{7}{ }^{7} \mathrm{Li}$ isotope shifts of the transition energies are determined.


Keywords: all-electron explicitly correlated Gaussian function, relativistic corrections for few-electron atoms, Rydberg spectrum of lithium atom
(Some figures may appear in colour only in the online journal)

## 1. Introduction

Since the beginning of quantum mechanics, quantitative studies of atomic energy levels have contributed many important results to the atomic physics and, in particular, atomic Rydberg systems [1]. The data obtained have enhanced our understanding of the atomic electronic structure and of other atomic properties. With the advancement of computational approaches, it has been possible to develop more accurate theoretical models for the electronic structure of atoms. Through experimental and theoretical studies, it has been shown that highly excited Rydberg atoms possess some unusual properties that can be controlled by state selection and the application of external

[^0]electromagnetic fields [2]. With the discovery of these properties in recent decades, new and interesting applications have been proposed for Rydberg atoms [3].

Back in 1982, Richard Feynman postulated that in order to accurately simulate the behavior of a quantum system in a reasonable amount of time, a new generation of computers called quantum computers needed to be built [4]. In recent decades, superconductors, trapped ions, quantum dots, neutral atoms, photons, and spins in solid-state hosts have been examined for use in quantum information processing [5, 6]. The use of neutral Rydberg atoms as qubits boasts several interesting characteristics. Atoms of a particular isotope of an element are quantum systems that can be readily prepared in well-defined, stable, and identical quantum states. Although the application of atoms is limited by the tunability of their properties, Rydberg atoms offer strong and tunable atomic
interactions that can be adjusted by selecting states with different principal quantum numbers or orbital angular momenta. These features make Rydberg atoms highly desirable candidates for the development of memory units for quantum computers [5-7].

The accuracy of the results obtained using theoretical models is influenced by two key factors. The first is related to the use of the Born-Oppenheimer ( BO ) approximation in the calculations. Due to the dependence of the properties of Rydberg atoms on the mass of the nucleus, the coupling of the motions of the nucleus and the electrons should be accounted for in high-accuracy calculations (see reference [6]), i.e. the BO approximation should not be assumed at the start of the calculations. To our knowledge, such non-BO high-accuracy atomic calculations have only been performed by our group $[8,9]$. The second key factor in achieving high-accuracy results from atomic calculations is the selection of an appropriate basis function for expanding the wave function of the studied states of the system. Explicitly correlated basis functions are likely to be the best choice for performing atomic groundand excited-state calculations. As such functions explicitly depend on inter-electron distances, they allow for a very accurate description of the electronic correlation effects. Hylleraastype (Hy) functions and explicitly correlated Gaussian (ECG) functions have been the most popular correlated basis functions used in high-accuracy atomic calculations. However, the former functions, despite their superb accuracy, cannot easily be extended to calculate the states of atomic systems with more than three electrons. The Gaussian functions do not have these limitations, but they are not as efficient as the Hy functions in describing the behavior of the wave function near the particle coalescence points, and have less favourable long range behavior. The deficiency of the Gaussian functions, that they do not fulfill the so-called Kato cusp conditions, can be remedied by using larger expansions of the wave function in terms of these functions. Employing a larger number of well-optimized basis functions to calculate the ground and excited atomic states not only improves the accuracy of the total atomic energy but also the accuracy of the expectation values of other important atomic properties. However, properties represented by operators with singularities may still show considerably worse convergence than that of the total energy. This, for example, applies to operators involving one- and two-electron Dirac delta functions, $\delta\left(\mathbf{r}_{i j}\right)$, and the operators describing the relativistic correction to the kinetic energy, which contain the fourth power of the linear momenta. The convergence rate of the expectation values of such operators with the number of basis functions may be significantly slower than the convergence of the expectation value of the Hamiltonian. In some cases, this slow convergence can be overcome by adopting regularization techniques that employ expectation value identities that allow a more accurate determination of the expectation values for the eigenstates of the Hamiltonian.

One of the aims of this work is to implement expectation value identities involving singular operators that appear in the calculation of the leading relativistic corrections for
atomic $P$ states. As mentioned above, the operator regularization approach accelerates the convergence of the expectation values of singular operators in terms of the number of basis functions. Thus, one can use an expansion of the wave function that already provides satisfactory convergence for the total energy, but not yet for the expectation value of a singular operator, to calculate its expectation value using an identity. That may be particularly important for highly excited states, where the basis set convergence usually becomes notably worse than for the lower-energy states.

Although some $P$ states of the lithium atom have been previously studied using explicitly correlated methods by other groups [10-28], those works have been limited to just a couple of the lowest states. There are only two works where highly excited $P$ states have been considered, one by the present authors [27] and one by Wang et al [29]. It is important to note that the use of the nonBO approach from the start (i.e. non-perturbatively) in the present calculations sets the present work apart from previous calculations by other groups, where the non-relativistic wave function and the corresponding energy were generally obtained by assuming an infinite mass of the nucleus, while the corrections due to the finite nuclear mass were calculated using perturbation theory. The use of the non-BO nonrelativistic wave function also facilitates the automatic inclusion of recoil effects when the relativistic corrections are computed.

## 2. Method

The basic all-electron ECG basis functions used to construct the $P$-state wave functions in the present work have the following form (for more information see references [30, 31]):

$$
\begin{equation*}
\phi_{k}=z_{i_{k}} \exp \left[-\mathbf{r}^{\prime}\left(A_{k} \otimes I_{3}\right) \mathbf{r}\right], \tag{1}
\end{equation*}
$$

where $\mathbf{r}$ is a $3 n$ vector column of the electron coordinates (referenced to the nucleus),

$$
\mathbf{r}=\left(\begin{array}{l}
\mathbf{r}_{1} \\
\mathbf{r}_{2} \\
\mathbf{r}_{3}
\end{array}\right)
$$

$z_{i_{k}}$ is the $z$-coordinate of the $i$ th electron, $i_{k}$ is an adjustable integer parameter (specific to each basis function $k$ ), $A_{k}$ is an $n \times n$ real symmetric matrix, $\otimes$ is the Kronecker product, and $I_{3}$ is a $3 \times 3$ identity matrix. The prime symbol denotes the matrix/vector transpose. The Gaussian basis function (1) is square integrable if matrix $A_{k}$ is positive definite. To assure this requirement, $A_{k}$ is represented by the Cholesky-factored form, $A_{k}=L_{k} L_{k}^{\prime}$, where $L_{k}$ is a lower triangular matrix. The $A_{k}$ matrix given in this form is always positive definite, regardless of the values of the $L_{k}$ matrix elements. Thus, the elements of $L_{k}$ can be varied without any constraints from $\infty$ to $-\infty$.

In the present calculations, we use the spin-free formalism to ensure the correct permutational symmetry properties. For this purpose, an appropriate permutational symmetry projector is constructed and applied to each
basis function (1). In constructing the symmetry projector, the standard procedure involving Young operators (see references [32,33]) is used. In the case of the ${ }^{2} P$ states of lithium, the permutation operator can be chosen in the form $Y=\left(1+P_{12}\right)\left(1-P_{23}\right)$, where $P_{i j}$ denotes the permutation of the spatial coordinates of the $i$ th and $j$ th electrons (particle 0 is the nucleus). More details about the generation of the wave function and its variational optimization can be found in references [27, 31].

In the nonrelativistic (nr) variational calculations, the Hamiltonian is obtained by separating the atom's center-of-mass motion from the nonrelativistic laboratory-frame Hamiltonian. This separation is rigorous and reduces the fourparticle problem of the Li atom to a three pseudoparticle problem represented by the following 'internal' Hamiltonian, expressed in terms of $\mathbf{r}_{i}$ 's (atomic units are assumed throughout):

$$
\begin{align*}
H_{\mathrm{nr}}^{\mathrm{int}}= & -\frac{1}{2}\left(\sum_{i=1}^{3} \frac{1}{\mu_{i}} \nabla_{\mathbf{r}_{i}}^{2}+\sum_{i=1}^{3} \sum_{j \neq i}^{3} \frac{1}{m_{0}} \nabla_{\mathbf{r}_{i}}^{\prime} \nabla_{\mathbf{r}_{j}}\right) \\
& +\sum_{i=1}^{3} \frac{q_{0} q_{i}}{\mathbf{r}_{i}}+\sum_{i=1}^{3} \sum_{j<i}^{3} \frac{q_{i} q_{j}}{\mathbf{r}_{i j}} . \tag{2}
\end{align*}
$$

Here, $q_{0}=3$ is charge of the nucleus, $q_{i}=-1(i=1,2,3)$ are the electron charges, $m_{0}$ is the nuclear mass ( $m_{0}=12786.3933$ for ${ }^{7} \mathrm{Li}$ and $m_{0}=10961.898$ for $\left.{ }^{6} \mathrm{Li}\right), \mu_{i}=m_{0} m_{i} /\left(m_{0}+m_{i}\right)$ is the reduced mass of the electron $i\left(m_{1}=m_{2}=m_{3}=1\right)$, and $r_{i j}=\left|\mathbf{r}_{j}-\mathbf{r}_{i}\right|$ are the distances between the (pseudo)electrons. The calculations involving the nonrelativistic Hamiltonian $H_{\mathrm{nr}}^{\mathrm{int}}$ can be carried out for both finite and infinite masses of the Li nucleus. They yield the nonrelativistic ground- and excitedstate energies ( $E_{\mathrm{nr}}$ ) and the corresponding wave functions. Both the energy and the wave function depend on the mass of the nucleus. In this work, we report both the finite-mass and infinite-mass results. The Hamiltonian (2) can also be conveniently written in a compact matrix form [8] as:

$$
\begin{equation*}
H_{\mathrm{nr}}^{\mathrm{int}}=-\nabla_{\mathbf{r}}^{\prime} \mathbf{M} \nabla_{\mathbf{r}}+\sum_{i=1}^{3} \frac{q_{0} q_{i}}{\mathbf{r}_{i}}+\sum_{i=1}^{3} \sum_{j<i}^{3} \frac{q_{i} q_{j}}{\mathbf{r}_{i j}}, \tag{3}
\end{equation*}
$$

where

$$
\nabla_{\mathbf{r}}=\left(\begin{array}{c}
\nabla_{\mathbf{r}_{1}} \\
\nabla_{\mathbf{r}_{2}} \\
\nabla_{\mathbf{r}_{3}}
\end{array}\right)
$$

is a nine-component gradient vector and $\mathbf{M}=M \otimes I_{3}$ is the Kronecker product of a $3 \times 3$ matrix $M$ and the $3 \times 3$ identity matrix $I_{3}$. The matrix $M$ has diagonal elements $1 /\left(2 \mu_{1}\right)$, $1 /\left(2 \mu_{2}\right)$, and $1 /\left(2 \mu_{3}\right)$, while all the off-diagonal elements are equal to $1 /\left(2 m_{0}\right)$.

The nonrelativistic energy, even obtained using a very accurate, well optimized wave function, is insufficient to calculate the total and transition energies of the atomic ground and excited states with an accuracy comparable to the available experimental results. The relativistic and quantum electrodynamics (QED) effects must also be included in the calculations. The approach that is the most practical and most
frquently used to account for the relativistic and QED effects in light atoms is to expand the total energy in powers of the fine-structure constant, $\alpha[34,35]$ :

$$
\begin{equation*}
E_{\mathrm{tot}}=E_{\mathrm{nr}}+\alpha^{2} E_{\mathrm{rel}}^{(2)}+\alpha^{3} E_{\mathrm{QED}}^{(3)}+\alpha^{4} E_{\mathrm{HQED}}^{(4)}+\ldots, \tag{4}
\end{equation*}
$$

where $E_{\mathrm{nr}}$ is the nonrelativistic energy of the state being considered, the second term, $\alpha^{2} E_{\text {rel }}^{(2)}$, represents the leading relativistic corrections, the third term, $\alpha^{3} E_{\mathrm{QED}}^{(3)}$, represents the leading QED corrections, and the fourth term, $\alpha^{4} E_{\mathrm{HQED}}^{(4)}$, represent the higher-order QED corrections. Each of these terms is evaluated as an expectation value of some effective operator that represents the calculated term. $E_{\text {rel }}^{(2)}$ is calculated as the expectation value of the Dirac-Breit Hamiltonian in the Pauli approximation, $H_{\text {rel }}[36,37]$. In this study, the relativistic correction for the $P$-states, $H_{\mathrm{rel}}$, contains the following terms:

$$
\begin{equation*}
H_{\mathrm{rel}}=H_{\mathrm{MV}}+H_{\mathrm{D}}+H_{\mathrm{OO}}+H_{\mathrm{SS}} \tag{5}
\end{equation*}
$$

where $H_{\mathrm{MV}}, H_{\mathrm{D}}, H_{\mathrm{OO}}$, and $H_{\text {SS }}$ are operators that are commonly interpreted as the mass-velocity, Darwin, orbit-orbit, and spin-spin corrections, respectively. The explicit form of these operators in the internal coordinates can be found in our previous works [38, 39]. It should be mentioned that, due to the use of a finite nuclear mass in the nonrelativistic Hamiltonian, the recoil effects are directly included in the calculations of the relativistic correction. In general, for non-singlet states of atoms, $H_{\text {rel }}$ should also contain a term describing the spin-orbit interaction. In this work, however, it was not included. The experimental data show that the fine-structured splits for the lithium atom are small. In fact, for the excited $n P$ states ( $n>2$ ) they get progressively smaller (a few hundredths of a wavenumber) and essentially vanish in the limit of high $n$. As we are primarily concerned with the energy levels and transitions between Rydberg states, the missing contribution due to the spin-orbit term is not expected to have a particularly notable effect on the accuracy of our calculations.

The $E_{\mathrm{QED}}^{(3)}$ term in (4) represents the leading QED correction. For an atomic system, it takes into account the twophoton exchange, the vacuum polarization, and the electron self-energy effects. The explicit form of the operator is:

$$
\begin{align*}
H_{\mathrm{QED}}= & \sum_{\substack{i, j=1 \\
j>i}}^{3}\left[\left(\frac{164}{15}+\frac{14}{3} \ln \alpha\right) \delta\left(\mathbf{r}_{i j}\right)-\frac{7}{6 \pi} \mathcal{P}\left(\frac{1}{r_{i j}^{3}}\right)\right] \\
& +\sum_{i=1}^{3}\left(\frac{19}{30}-2 \ln \alpha-\ln k_{0}\right) \frac{4 q_{0}}{3} \delta\left(\mathbf{r}_{i}\right) \tag{6}
\end{align*}
$$

where the first sum represents the Araki-Sucher term [11, 40-43], while the principal value $\mathcal{P}\left(1 / r_{i j}^{3}\right)$ is defined as:

$$
\begin{equation*}
\left\langle\mathcal{P}\left(\frac{1}{r_{i j}^{3}}\right)\right\rangle=\lim _{a \rightarrow 0}\left\langle\frac{1}{r_{i j}^{3}} \Theta\left(r_{i j}-a\right)+4 \pi(\gamma+\ln a) \delta\left(\mathbf{r}_{i j}\right)\right\rangle . \tag{7}
\end{equation*}
$$

In the last expression, $\Theta(\ldots)$ is the Heaviside step function and $\gamma=0.577215 \ldots$ is the Euler-Mascheroni constant.

The dominant part of the electron self-energy is the socalled Bethe logarithm, $\ln k_{0}$, which appears in expression (6).

Table 1. Comparison of the convergence of the expectation values of some singular operators for three selected Rydberg states of ${ }^{\infty} \mathrm{Li}$ computed using the regularization technique (marked with a tilde) and using direct calculations (no tilde). All values are in atomic units.

| State | Basis | $\left\langle\tilde{H}_{\mathrm{MV}}\right\rangle$ | $\left\langle H_{\mathrm{MV}}\right\rangle$ | $\left\langle\tilde{\delta}\left(\mathbf{r}_{i}\right)\right\rangle$ | $\left\langle\delta\left(\mathbf{r}_{i}\right)\right\rangle$ | $\left\langle\tilde{\delta}\left(\mathbf{r}_{i j}\right)\right\rangle$ | $\left\langle\delta\left(\mathbf{r}_{i j}\right)\right\rangle$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $1 s^{2} 2 p^{1}$ | 6000 | -77.505654 | -77.503986 | 4.558732346 | 4.558617001 | 0.177424699 | 0.177432409 |
|  | 7000 | -77.505640 | -77.504338 | 4.558732348 | 4.558643190 | 0.177424700 | 0.177429516 |
|  | 8000 | -77.505630 | -77.505072 | 4.558732350 | 4.558693976 | 0.177424700 | 0.177427586 |
|  | 9000 | -77.505624 | -77.505244 | 4.558732350 | 4.558705279 | 0.177424700 | 0.177426306 |
| Ref. [28] | 33600 | $-77.50561673(9)$ |  | $4.55873235019(2)$ |  | $0.1774246999(1)$ |  |
| $1 s^{2} 7 p^{1}$ | 9000 | -77.634311 | -77.626752 | 4.567779196 | 4.567246971 | 0.177896659 | 0.177961446 |
|  | 10000 | -77.634174 | -77.628321 | 4.567779250 | 4.567365639 | 0.177896676 | 0.177934245 |
|  | 11000 | -77.634056 | -77.630790 | 4.567779286 | 4.567550718 | 0.177896682 | 0.177911928 |
|  | 12000 | -77.634043 | -77.631901 | 4.567779296 | 4.567625944 | 0.177896683 | 0.177907462 |
| $1 s^{2} 12 p^{1}$ | 13000 | -77.637128 | -77.593046 | 4.567955622 | 4.564247289 | 0.177904856 | 0.178139915 |
|  | 14000 | -77.636807 | -77.595332 | 4.567956970 | 4.564559712 | 0.177905063 | 0.178068158 |
|  | 15000 | -77.636775 | -77.603093 | 4.567958235 | 4.565213610 | 0.177905145 | 0.178047780 |
|  | 16000 | -77.636757 | -77.608466 | 4.567959099 | 4.565627984 | 0.177905199 | 0.178037245 |

The main difficulty in computing the QED term for a multielectron atomic system is to accurately calculate $\ln k_{0}$. It is known that the dominant contribution to $\ln k_{0}$ comes from the inner shell electrons. Therefore, at the lowest level of the approximation, the value of the Bethe logarithm determined for the $1 s^{2} 2 p^{1}$ state of the Li atom may be used to calculate the QED corrections for the higher states of this system. The Bethe logarithm for the Li $1 s^{2} 2 p^{1}$ state was calculated by Yan et al [21] and is adopted in our current calculations for all the $P$ states considered.

The $E_{\mathrm{HQED}}^{(4)}$ term in expansion (4) is computed as an expectation value of the following approximate operator derived by Pachucki and Komasa [44, 45]:

$$
\begin{equation*}
H_{\mathrm{HQED}}=\pi q_{0}^{2}\left(\frac{427}{96}-2 \ln 2\right) \sum_{i=1}^{3} \delta\left(\mathbf{r}_{i}\right) \tag{8}
\end{equation*}
$$

$E_{\text {HOED }}^{(4)}$ includes the dominant electron-nucleus one-loop radiative correction. The two-loop radiative, electron-electron radiative, and higher-order relativistic corrections are neglected. The above expression only provides a raw estimate of $E_{\mathrm{HQED}}^{(4)}$. It seems that, based on the available data for smaller atoms, one can expect that it should capture the bulk of the higher-order QED effects with an overall error that is likely to be less than $50 \%$.

It should be noted that the expectation values of both the $H_{\mathrm{QED}}$ and $H_{\text {HQED }}$ Hamiltonians are calculated in this work with the infinite-nuclear-mass wave functions, because the corresponding formalism was developed under the assumption of a clamped nucleus [44, 45]. Hence, no recoil effects are included in the $E_{\mathrm{QED}}^{(3)}$ and $E_{\mathrm{HQED}}^{(4)}$ computed in this work.

Some of the aforementioned operators include singular terms. For instance, $H_{\mathrm{MV}}$ contains the terms proportional to $\nabla_{\mathbf{r}_{i}}^{4}$ and $H_{\mathrm{D}}, H_{\mathrm{SS}}, H_{\mathrm{QED}}$, and $H_{\mathrm{HQED}}$ include singular oneand two-electron Dirac delta functions, $\delta\left(\mathbf{r}_{i}\right)$ and $\delta\left(\mathbf{r}_{i j}\right)$ (note that $\left.\delta\left(\mathbf{r}_{i}\right) \equiv \delta\left(x_{i}\right) \delta\left(y_{i}\right) \delta\left(z_{i}\right)\right)$. The expectation values of these operators usually converge rather slowly with the number of the basis functions used to expand the wave function. While
there are multiple factors that contribute to the slow convergence, the main reason for this deficiency is related to the fact that with these operators, the expectation values sample the wave function locally (e.g. in the subspace where $\mathbf{r}_{i}=0$ ) rather than globally in the entire coordinate space. The approximate nonrelativistic wave function may have a local error that is considerably more significant than the global error in the energy expectation value, which largely cancels out due to the nature of the variational method (this behavior is general and occurs for any basis set employed). There have been studies that aimed to transform the singular operators to more global operators to accelerate the convergence of the expectation values calculated with those operators with the number of basis functions [46-51]. A rather practical approach was proposed by Drachman [51] based on the work of Trivedi [50]. The Drachman approach has been adopted in quite a few works in recent decades; it makes use of an expectation value identity. For exact eigenfunctions, the approach gives the same expectation values as when the singular (non-global) operator is used. At the same time, for approximate wave functions, as the studies performed so far have demonstrated, the use of the expectation value identity facilitates a considerable improvement of the convergence of the expectation values of the singular operators that appear in the operators representing the leading relativistic corrections [39, 52].

The use of the Drachman method [51] (which may be referred to as a regularization technique) has been very effective not only for Gaussian basis functions but also for other types of function [20, 28]. However, due to the improper behavior of the Gaussian functions (1) in the vicinity of particle coalescence points and due to the fact that they do not satisfy the Kato cusp conditions [53], improving the convergence of the expectation values of singular operators calculated using Gaussians is particularly important. Even though the poor convergence can be remedied to some degree by simply using larger Gaussian basis sets, adopting the regularization technique clearly brings great benefits [51, 52].

Table 2. Convergence of the nonrelativistic variational energy $\left(E_{\mathrm{nr}}\right)$, the mass-velocity correction $\left(H_{\mathrm{MV}}\right)$, and the expectation values of the one- and two-electron Dirac $\delta$-functions with the number of basis functions for the lowest twelve ${ }^{2} P$ states of the lithium atom. The numbers in parentheses are estimated uncertainties due to the basis truncation. All values are in atomic units. In references [28,29] the variational calculations were performed using the Hy-type basis functions.

| State | Isotope | Basis | $E_{\text {nr }}$ | $\left\langle\tilde{H}_{\mathrm{MV}}\right\rangle$ | $\left\langle\tilde{\delta}\left(\mathbf{r}_{i}\right)\right\rangle$ | $\left\langle\tilde{\delta}\left(\mathbf{r}_{i j}\right)\right\rangle$ | $\left\langle H_{\mathrm{OO}}\right\rangle$ | $\left\langle\mathcal{P}\left(1 / r_{i j}^{3}\right)\right\rangle$ | $E_{\text {tot }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $1 s^{2} 2 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 6000 | -7.409 55775865 | -77.480954 | 4.557646046 | 0.177384817 | -0.406154 192 |  | -7.410 07185621 |
|  |  | 7000 | -7.409 55775881 | -77.480940 | 4.557646048 | 0.177384818 | -0.406154 190 |  | -7.41007185577 |
|  |  | 8000 | -7.409 55775895 | -77.480931 | 4.557646050 | 0.177384818 | -0.406154 189 |  | -7.41007185552 |
|  |  | 9000 | -7.409 55775900 | -77.480925 | 4.557646051 | 0.177384818 | -0.406154 189 |  | -7.41007185527 |
|  |  | $\infty$ | -7.409557 7592(1) |  |  |  |  |  | -7.410071 8550(2) |
|  |  | 9000 | -7.409 45811056 | $-77.476815$ | 4.557465283 | 0.177378181 | -0.407 772896 |  | -7.409 97221363 |
|  | $\begin{gathered} { }^{6} \mathrm{Li} \\ { }^{\infty} \mathrm{Li} \end{gathered}$ | $\infty$ | -7.409 4581108 (1) |  |  |  |  |  | -7.409 972 2133(2) |
|  |  | 9000 | -7.410 15653263 | $-77.505624$ | 4.558732350 | 0.177424700 | $-0.396425741$ | 9.63211 | -7.41067058837 |
|  |  | $\infty$ | -7.410 1565329 (1) |  |  |  |  |  | -7.410670 5881(2) |
| Ref. [28] |  | 33600 | -7.410 15653265241 (3) | -77.505 61673(9) | $4.55873235019(2)$ | $0.1774246999(1)$ |  |  |  |
| $1 s^{2} 3 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 6000 | -7.33655636316 | -77.574 185 | 4.564054035 | 0.177726312 | $-0.427812412$ |  | -7.33707141337 |
|  |  | 7000 | -7.33655636359 | $-77.574143$ | 4.564054043 | 0.177726313 | $-0.427812401$ |  | -7.33707141200 |
|  |  | 8000 | -7.33655636363 | $-77.574121$ | 4.564054045 | 0.177726314 | -0.427 812399 |  | -7.33707141107 |
|  |  | 9000 | -7.33655636369 | -77.574 120 | 4.564054045 | 0.177726314 | -0.427 812399 |  | -7.33707141108 |
|  |  | $\infty$ | -7.3365563639(1) |  |  |  |  |  | -7.337071 4095(8) |
|  | ${ }^{6} \mathrm{Li}$ | 9000 | $-7.33645728572$ | -77.570 013 | 4.563873525 | 0.177719697 | $-0.429434639$ |  | -7.33697233919 |
|  |  | $\infty$ | -7.336457 2859(1) |  |  |  |  |  | -7.336972 3374(9) |
|  | ${ }^{\infty} \mathrm{Li}$ | 9000 | -7.33715170858 | -77.598803 | 4.565138855 | 0.177766074 | $-0.418062732$ | 6.98868 | -7.33766671460 |
|  |  | $\infty$ | -7.3371517088(1) |  |  |  |  |  | $-7.3376667130(8)$ |
| $1 s^{2} 4 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 7000 | -7.31129510102 | -77.596593 | 4.565703912 | 0.177808781 | -0.433 510657 |  | -7.31181032077 |
|  |  | 8000 | -7.31129510152 | -77.596524 | 4.565703924 | 0.177808784 | -0.433 510637 |  | $-7.31181031825$ |
|  |  | 9000 | -7.31129510157 | -77.596505 | 4.565703926 | 0.177808784 | -0.433510635 |  | -7.31181031748 |
|  |  | 10000 | -7.31129510164 | -77.596502 | 4.565703927 | 0.177808784 | -0.433 510635 |  | -7.31181031735 |
|  |  | $\infty$ | -7.311295 1021(2) |  |  |  |  |  | -7.3118103162(6) |
| Ref. [29] | ${ }^{6} \mathrm{Li}$ | $\infty$ | -7.3112951016176(2) |  |  |  |  |  |  |
|  |  | 10000 | -7.31119625424 | -77.592395 | 4.565523453 | 0.177802172 | -0.435 133712 |  | -7.31171147692 |
|  |  | $\infty$ | $-7.3111962547(2)$ |  |  |  |  |  | -7.3117114758(6) |
| Ref. [29] |  | $\infty$ | $-7.3111962542635(2)$ |  |  |  |  |  |  |
|  | ${ }^{\infty} \mathrm{Li}$ | 10000 | -7.311889 06073 | -77.621 182 | 4.566788460 | 0.177848521 | -0.423 755946 | 6.36358 | -7.31240423487 |
|  |  | $\infty$ | -7.311889 0612(2) |  |  |  |  |  | -7.312404 2338(6) |
| Ref. [29] |  | 22302 | -7.31188906075855 |  |  |  |  |  |  |
| Ref. [29] |  | $\infty$ | -7.311889 $0607587(2)$ |  |  |  |  |  |  |
| $1 s^{2} 5 p^{1}$ | ${ }^{7} \mathrm{Li}$ |  | -7.299 69490200 |  |  |  | -0.435 573946 |  | -7.300 21016590 |
|  |  | 8000 | -7.29969490221 | -77.604304 | 4.566297883 | 0.177837806 | -0.435 573942 |  | -7.300 21016568 |
|  |  | 9000 | -7.299 69490227 | -77.604 296 | 4.566297884 | 0.177837806 | -0.435 573942 |  | -7.30021016538 |
|  |  | 10000 | -7.29969490235 | -77.604 290 | 4.566297885 | 0.177837806 | -0.435 573941 |  | -7.300 21016518 |
|  |  | $\infty$ | -7.299694 9026(1) |  |  |  |  |  | -7.3002101658(3) |


| Ref. [29] | ${ }^{6} \mathrm{Li}$ | $\infty$ | -7.299 694902339 30(6) |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 10000 $\infty$ | $\begin{aligned} & -7.29959617062 \\ & -7.2995961709(1) \end{aligned}$ | -77.600 184 | 4.566117425 | 0.177831195 | -0.437197305 |  | $\begin{aligned} & -7.30011144044 \\ & -7.3001114399(4) \end{aligned}$ |
| Ref. [29] |  | $\infty$ | -7.29959617066065(5) |  |  |  |  |  |  |
|  | ${ }^{\infty} \mathrm{Li}$ | 10000 | $-7.30028816622$ | -77.628970 | 4.567382335 | 0.177877536 | $-0.425817528$ | 6.10829 | $\begin{gathered} -7.30080338741 \\ -7.3008033880(3) \end{gathered}$ |
|  |  | $\infty$ | -7.300288 1665(2) |  |  |  |  |  |  |
| Ref. [29] |  | 22302 | -7.30028816626505 |  |  |  |  |  |  |
| Ref. [29] |  | $\infty$ | -7.300 2881662651 (1) |  |  |  |  |  |  |
| $1 s^{2} 6 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 8000 | -7.293 42718742 | -77.607658 | 4.566561030 | 0.177850526 | -0.436490373 |  | -7.29394246683 |
|  |  | 9000 | -7.293 42718761 | -77.607653 | 4.566561044 | 0.177850527 | -0.436490 366 |  | -7.29394246696 |
|  |  | 10000 | -7.293 42718768 | -77.607649 | 4.566561047 | 0.177850527 | -0.436490 365 |  | -7.29394246689 |
|  |  | 11000 | -7.293 42718778 | -77.607648 | 4.566561049 | 0.177850527 | -0.436490 365 |  | -7.29394246690 |
|  |  | $\infty$ | -7.293 427 1880(1) |  |  |  |  |  | -7.293942 4673(2) |
| Ref. [29] |  | $\infty$ | -7.293 4271878104 (4) |  |  |  |  |  |  |
|  | ${ }^{6} \mathrm{Li}$ | 11000 | -7.29332852201 | -77.603 542 | 4.566380594 | 0.177843917 | $-0.438113854$ |  | -7.29384380812 |
|  |  | $\infty$ | -7.293328 5223(1) |  |  |  |  |  | -7.293843 8076(2) |
| Ref. [29] |  | $\infty$ | -7.293 $3285220817(4)$ |  |  |  |  |  |  |
|  | ${ }^{\infty} \mathrm{Li}$ | 11000 | -7.294020055 29 | -77.632327 | 4.567645466 | 0.177890254 | $-0.426733210$ | 6.03559 | $\begin{gathered} -7.29453529275 \\ -7.2945352931(2) \end{gathered}$ |
|  |  | $\infty$ | -7.294020 0556(1) |  |  |  |  |  |  |
| Ref. [29] |  | 22302 | -7.29402005537765 |  |  |  |  |  |  |
| Ref. [29] |  | $\infty$ | -7.294020055 3779(3) |  |  |  |  |  |  |
| $1 s^{2} 7 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 9000 | -7.289 66228912 | -77.609 632 | 4.566694794 | 0.177856934 | -0.436957 281 |  | -7.290 17758878 |
|  |  | 10000 | -7.289662 29125 | -77.609 495 | 4.566694848 | 0.177856950 | -0.436957 145 |  | -7.290 17758462 |
|  |  | 11000 | -7.289662 29166 | -77.609377 | 4.566694886 | 0.177856957 | -0.436957 092 |  | -7.290 17757971 |
|  |  | 12000 | -7.289 66229186 | -77.609364 | 4.566694895 | 0.177856958 | -0.436957 083 |  | -7.290 17757936 |
|  |  | $\infty$ | -7.289662 2932(7) |  |  |  |  |  | -7.290 177 5775(9) |
| Ref. [29] |  | $\infty$ | -7.289662 $291990(2)$ |  |  |  |  |  |  |
|  | ${ }^{6} \mathrm{Li}$ | 12000 | -7.289563 66715 | -77.605 257 | 4.566514443 | 0.177850347 | $-0.438580632$ |  | -7.290 07896164 |
|  |  | $\infty$ | -7.289563 6686(7) |  |  |  |  |  | -7.290 078 9598(9) |
| Ref. [29] |  | $\infty$ | -7.289563 667321 (2) |  |  |  |  |  |  |
|  | ${ }^{\infty} \mathrm{Li}$ | 12000 | -7.29025491262 | $-77.634043$ | 4.567779296 | 0.177896683 | -0.427 199558 | 5.91039 | $\begin{aligned} & -7.29077015844 \\ & -7.2907701566(9) \end{aligned}$ |
|  |  | $\infty$ | -7.290254 9140(7) |  |  |  |  |  |  |
| Ref. [29] |  | 22302 | -7.29025491279716 |  |  |  |  |  |  |
| Ref. [29] |  | $\infty$ | -7.290254912799(2) |  |  |  |  |  |  |
| $1 s^{2} 8 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 11000 | -7.28722561901 | -77.610 699 | 4.566769796 | 0.177860503 | -0.437219 592 |  | -7.28774092822 |
|  |  | 12000 | -7.287225620 18 | -77.610 694 | 4.566769821 | 0.177860505 | -0.437219 563 |  | -7.28774092916 |
|  |  | 13000 | -7.28722562280 | -77.610 554 | 4.566769948 | 0.177860533 | -0.437219301 |  | -7.28774092524 |
|  |  | 14000 | -7.287225623 27 | -77.610345 | 4.566769963 | 0.177860551 | -0.437219 125 |  | -7.28774091624 |
|  |  | $\infty$ | -7.287225 6241(4) |  |  |  |  |  | -7.287740 9146(8) |

Table 2. Continue

| Ref. [29] |  | $\infty$ | -7.287225 623 6354(6) |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | ${ }^{6} \mathrm{Li}$ | 14000 $\infty$ | $\begin{gathered} -7.28712702581 \\ -7.2871270266(4) \end{gathered}$ | -77.606239 | 4.566589512 | 0.177853941 | $-0.438842709$ |  | $\begin{gathered} -7.28764232578 \\ -7.2876423241(8) \end{gathered}$ |
| Ref. [29] |  | $\infty$ | -7.2871270262255(6) |  |  |  |  |  |  |
|  | ${ }^{\infty} \mathrm{Li}$ | 14000 | -7.287818080 19 | -77.635 024 | 4.567854357 | 0.177900275 | $-0.427461394$ | 5.78497 | -7.28833333149 |
|  |  | $\infty$ | -7.287818 0810(4) |  |  |  |  |  | -7.288333 3298(8) |
| Ref. [29] |  | 22302 | -7.287818080615 15 |  |  |  |  |  |  |
| Ref. [29] |  | $\infty$ | -7.287818 $0806158(6)$ |  |  |  |  |  |  |
| $1 s^{2} 9 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 12000 | -7.285 55867173 | -77.611430 | 4.566814785 | 0.177862604 | -0.437378387 |  | -7.286 07399066 |
|  |  | 13000 | -7.285 55867494 | -77.611297 | 4.566814876 | 0.177862633 | -0.437378 126 |  | -7.28607398762 |
|  |  | 14000 | -7.285 55867657 | -77.611276 | 4.566814921 | 0.177862643 | -0.437378 059 |  | -7.28607398828 |
|  |  | 15000 | -7.285 55868328 | -77.611200 | 4.566815206 | 0.177862671 | -0.437377805 |  | -7.28607399130 |
|  |  | $\infty$ | -7.285 558 6849(8) |  |  |  |  |  | -7.286073 9930(9) |
| Ref. [29] |  | $\infty$ | -7.285 $5586856755(5)$ |  |  |  |  |  |  |
|  | ${ }^{6} \mathrm{Li}$ | 15000 | -7.285 46010483 | -77.607 093 | 4.566634756 | 0.177856061 | $-0.439001410$ |  | -7.28597541984 |
|  |  | $\infty$ | -7.285 $4601027(9)$ |  |  |  |  |  | -7.285 9754216 (9) |
| Ref. [29] |  | $\infty$ | -7.285 $4601072730(5)$ |  |  |  |  |  |  |
|  | ${ }^{\infty} \mathrm{Li}$ | 15000 | -7.28615102597 | -77.635 879 | 4.567899596 | 0.177902395 | -0.427 619948 | 5.16860 | -7.28666629231 |
|  |  | $\infty$ | -7.286151 0277(8) |  |  |  |  |  | -7.286666 2940(9) |
| Ref. [29] |  | 22302 | -7.286151028 42333 |  |  |  |  |  |  |
| Ref. [29] |  | $\infty$ | -7.2861510284238(5) |  |  |  |  |  |  |
| $1 s^{2} 10 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 13000 | -7.284 36837868 | -77.611863 | 4.566843800 | 0.177863950 | $-0.437479803$ |  | -7.284 88370235 |
|  |  | 14000 | -7.28436838366 | -77.611544 | 4.566843959 | 0.177864051 | $-0.437478855$ |  | -7.284 88369252 |
|  |  | 15000 | -7.28436838615 | -77.611471 | 4.566844073 | 0.177864068 | $-0.437478715$ |  | -7.284 88369157 |
|  |  | 16000 | -7.284368389 00 | -77.611425 | 4.566844119 | 0.177864079 | $-0.437478637$ |  | -7.284 88369233 |
|  |  | $\infty$ | -7.284368391(1) |  |  |  |  |  | -7.284883 6934(5) |
| Ref. [29] |  | $\infty$ | -7.284368393 1451(9) |  |  |  |  |  |  |
|  | ${ }^{6} \mathrm{Li}$ | 16000 | -7.284 26982432 | -77.607318 | 4.566663669 | 0.177857468 | -0.439 102257 |  | -7.284785 13465 |
|  |  | $\infty$ | -7.284 $269827(1)$ |  |  |  |  |  | -7.284785 1336(5) |
| Ref. [29] |  | $\infty$ | -7.284 $2698285171(9)$ |  |  |  |  |  |  |
|  | ${ }^{\infty} \mathrm{Li}$ | 16000 | -7.284 96064891 | -77.636104 | 4.567928509 | 0.177903802 | $-0.427720693$ | 5.43184 | -7.285 47591055 |
|  |  | $\infty$ | -7.284 $960651(1)$ |  |  |  |  |  | -7.285 475 9088(9) |
| Ref. [29] |  | 22302 | -7.284 96065310864 |  |  |  |  |  |  |
| Ref. [29] |  | $\infty$ | -7.284960653 1095(9) |  |  |  |  |  |  |


| $\overline{s^{2} 11 p^{1}}$ | ${ }^{7} \mathrm{Li}$ | 13000 | -7.283 48887934 | -77.612374 | 4.566861197 | 0.177864612 | -0.437549412 |  | -7.284004 21767 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 14000 | -7.283 48890037 | -77.611768 | 4.566862206 | 0.177864894 | -0.437546891 |  | -7.284004 20939 |
|  |  | 15000 | -7.283 48891202 | -77.611760 | 4.566862672 | 0.177864930 | -0.437546653 |  | -7.284004 22055 |
|  |  | 16000 | -7.283 48892497 | $-77.611725$ | 4.566862981 | 0.177864954 | -0.437546529 |  | -7.284004 23179 |
|  |  | $\infty$ | -7.283488 939(7) |  |  |  |  |  | -7.284004 241(5) |
|  | ${ }^{6} \mathrm{Li}$ | 16000 | $-7.28339037060$ | $-77.607618$ | 4.566682529 | 0.177858344 | -0.439 170164 |  | -7.284 59638809 |
|  |  | $\infty$ | $-7.283390385(7)$ |  |  |  |  |  | -7.283 905 692(4) |
|  | ${ }^{\infty} \mathrm{Li}$ | 16000 | $-7.28408112297$ | -77.636404 | 4.567947381 | 0.177904678 | $-0.427788490$ | 5.19768 | -7.284 59638809 |
|  |  | $\infty$ | $-7.284081137(8)$ |  |  |  |  |  | -7.284596398(5) |
| $1 s^{2} 12 p^{1}$ | ${ }^{7} \mathrm{Li}$ | 13000 | -7.282820 66248 | -77.612 449 | 4.566871208 | 0.177865132 | -0.437595440 |  | -7.283 33599897 |
|  |  | 14000 | -7.28282070279 | $-77.612128$ | 4.566872561 | 0.177865338 | -0.437594 125 |  | -7.283 33602322 |
|  |  | 15000 | -7.282820 73097 | -77.612096 | 4.566873828 | 0.177865421 | -0.437593890 |  | -7.283 33604931 |
|  |  | 16000 | -7.28282076649 | -77.612078 | 4.566874695 | 0.177865475 | -0.437593 832 |  | -7.283 33608344 |
|  |  | $\infty$ | $-7.28282083(3)$ |  |  |  |  |  | $-7.28333613(3)$ |
|  | ${ }^{6} \mathrm{Li}$ | 16000 | $-7.28272222002$ | -77.607971 | 4.566694242 | 0.177858865 | -0.439 217485 |  | -7.283 23754396 |
|  |  | $\infty$ | $-7.28272229(3)$ |  |  |  |  |  | $-7.28323760(3)$ |
|  | ${ }^{\infty} \mathrm{Li}$ | 16000 | -7.28341291703 | $-77.636757$ | 4.567959099 | 0.177905199 | $-0.427835690$ | 4.78042 | -7.283 92819228 |
|  |  | $\infty$ | -7.283 $41298(3)$ |  |  |  |  |  | -7.283 $92824(3)$ |

In this work, in the calculation of the expectation values of the delta functions expressed in terms of the internal coordinates, we employ the following Drachman identities:

$$
\begin{equation*}
\langle\psi| \delta\left(\mathbf{r}_{i}\right)|\psi\rangle=\frac{\mu_{i}}{\pi}\left[\langle\psi| \frac{E-V}{r_{i}}|\psi\rangle-\left\langle\nabla_{\mathbf{r}} \psi\right| \frac{\mathbf{M}}{r_{i}}\left|\nabla_{\mathbf{r}} \psi\right\rangle\right], \tag{9}
\end{equation*}
$$

$\langle\psi| \delta\left(\mathbf{r}_{i j}\right)|\psi\rangle=\frac{\mu_{i j}}{\pi}\left[\langle\psi| \frac{E-V}{r_{i}}|\psi\rangle-\left\langle\nabla_{\mathbf{r}} \psi\right| \frac{\mathbf{M}}{r_{i j}}\left|\nabla_{\mathbf{r}} \psi\right\rangle\right]$.
In the above expressions, $\mu_{i j} \equiv m_{i} m_{j} /\left(m_{i}+m_{j}\right)$ is the reduced mass, $V$ is the potential energy operator, and $E$ is the variational energy of the state under consideration (the expectation value of $H_{\mathrm{nr}}^{\mathrm{int}}$ ). Due to the absence of singular operators on the right-hand sides of expressions (9) and (10), the convergence of these expectation values is considerably faster.

A slow convergence rate with respect to the number of basis function also takes place for $H_{\mathrm{Mv}}$. In internal coordinates, this operator can be written in the following matrix form:

$$
\begin{equation*}
H_{\mathrm{MV}}=-\left(\nabla_{\mathbf{r}}^{\prime} \beta_{0} \mathbf{J} \nabla_{\mathbf{r}}\right)^{2}-\sum_{i=1}^{3}\left(\nabla_{\mathbf{r}}^{\prime} \beta_{i} \mathbf{J}_{i i} \nabla_{\mathbf{r}}\right)^{2} \tag{11}
\end{equation*}
$$

where $\beta_{0}=1 / \sqrt{8 m_{0}^{3}}, \quad \beta_{i}=1 / \sqrt{8 m_{i}^{3}}, \quad \mathbf{J}=\left(J \otimes I_{3}\right), \quad \mathbf{J}_{i i}=$ $J_{i i} \otimes I_{3}, J$ is a $3 \times 3$ matrix with all its elements equal to 1 , and $J_{i i}$ is a $3 \times 3$ matrix that has only one nonzero element, $\left(J_{i i}\right)_{i i}=1$. In the calculations of the expectation value of $H_{\mathrm{MV}}$, we adopted the following identity that is applicable to systems with arbitrary masses of constituent particles:

$$
\begin{align*}
\langle\psi| H_{\mathrm{MV}}|\psi\rangle=- & \lambda^{2}\langle\psi|(E-V)^{2}|\psi\rangle \\
& -\lambda^{2}\langle\psi|(E-V)\left(\nabla_{\mathbf{r}}^{\prime} \mathbf{B} \nabla_{\mathbf{r}}\right)|\psi\rangle \\
& +\lambda^{2}\langle\psi|\left(\nabla_{\mathbf{r}}^{\prime} \mathbf{M} \nabla_{\mathbf{r}}\right)^{2}|\psi\rangle \\
& +\lambda^{2}\langle\psi|\left(\nabla_{\mathbf{r}}^{\prime} \mathbf{M} \nabla_{\mathbf{r}}\right)\left(\nabla_{\mathbf{r}}^{\prime} \mathbf{B} \nabla_{\mathbf{r}}\right)|\psi\rangle \\
& -\beta_{0}\langle\psi|\left(\nabla_{\mathbf{r}}^{\prime} \mathbf{J} \nabla_{\mathbf{r}}\right)^{2}|\psi\rangle-\sum_{i=1}^{n} \beta_{i}\langle\psi|\left(\nabla_{\mathbf{r}}^{\prime} \mathbf{J}_{i i} \nabla_{\mathbf{r}}\right)^{2}|\psi\rangle . \tag{12}
\end{align*}
$$

The parameter $\lambda$ and the matrix $\mathbf{B}=B \otimes I_{3}$ in the above formula are chosen in such a way that the element(s) of the diagonal matrix $B$ corresponding to the lightest particle(s) in the system vanish. For instance, if particle $k$ is the lightest in the system (e.g. the particle is an electron) then we have

$$
\begin{equation*}
\lambda^{2}=\frac{\beta_{0}^{2}+\beta_{k}^{2}}{(M)_{k k}^{2}} \tag{13}
\end{equation*}
$$

and the diagonal elements of $B$ are;

$$
\begin{equation*}
(B)_{i i}=\frac{\beta_{0}^{2}+\beta_{k}^{2}}{\lambda^{2}(M)_{i i}}-(M)_{i i} \tag{14}
\end{equation*}
$$

When the difference between the mass of the lightest particle $\left(m_{k}\right)$ and the masses of the other particles in the system ( $m_{0}$ in the present case) is significant, the right-hand side of expression (12) converges to the exact limit considerably faster upon increasing the size of the basis. This will be demonstrated by the data given in the next section.

Table 3. The convergence of the total nonrelativistic energies of the lowest ${ }^{2} P$ state of ${ }^{6} \mathrm{Li},{ }^{7} \mathrm{Li}$, and ${ }^{\infty} \mathrm{Li}$ with the number of ECG basis functions. All energies are in a.u.

| Isotope | Basis | $E_{\text {nr }}$ |
| :--- | :---: | :---: |
| ${ }^{6} \mathrm{Li}$ | 10000 | -7.40945811056884 |
|  | 11000 | -7.40945811057031 |
|  | 12000 | -7.40945811057204 |
|  | 12500 | -7.40945811057284 |
|  | 13000 | -7.40945811057349 |
|  | 13500 | -7.40945811057397 |
| ${ }^{7} \mathrm{Li}$ | 10000 | -7.40955775901166 |
|  | 11000 | -7.40955775901313 |
|  | 12000 | -7.40955775901487 |
|  | 12500 | -7.40955775901566 |
|  | 13000 | -7.40955775901630 |
| ${ }^{2} \mathrm{Li}$ | 13500 | -7.4101565326468647 |
|  | 10000 | -7.41015653264398 |
|  | 11000 | -7.41015653264655 |
|  | 12000 | -7.41015653264720 |
|  | 12500 | -7.41015653264770 |
|  | 13000 | -7.41015653264790 |
|  | 13500 | $-7.41015653265241(3)$ |
| Ref. [28] ${ }^{\text {b }}$ | $13500^{\mathrm{a}}$ |  |

${ }^{\text {a }}$ The variational optimization of the ECG nonlinear parameters is performed for the infinite nuclear mass
${ }^{\mathrm{b}}$ Variational calculations are performed with Hy-type basis functions.

## 3. Results

The ground state $\left(1 s^{2} 2 p^{1}\right)$ of the lithium atom has been studied extensively by various groups over the last two decades [10-28]. Most of these studies reported results concerning only one or a few of the lowest $P$ states, however. Within an explicitly correlated approach, the higher excited states of lithium were studied by the present authors (up to the $1 s^{2} 10 p^{1}$ state) [27] and Wang et al (up to the $1 \mathrm{~s}^{2} 10 \mathrm{p}^{1}$ state) [29]. In the present calculations of the ${ }^{2} P$ states of lithium, the number of ECG basis functions for each state is significantly increased, compared to those used in the previous calculations [27]. Furthermore, the number of computed ${ }^{2} P$ states of lithium that we consider is extended to eleven (up to the state $1 s^{2} 12 p^{1}$ ). Importantly, in this work, we implemented and used a regularization method for calculating the expectation values of singular operators.

The calculations performed using the regularization method allow the estimation of its efficiency. Two aspects related to the efficiency can be examined. First, the higher excited states normally require the use of more basis functions in the calculations in order to describe the increasing number of radial nodes of the wave function. However, there are practical limits to the number of basis functions one can include in the calculations, which are constrained by the available computational resources. Therefore, the accuracy of the results achieved for the lower states is usually somewhat better than for the higher states, even if more basis functions are used in the calculation of the latter states. This decrease in the accuracy affects the expectation values of such global operators as the Hamiltonian less than the quantities represented by singular
operators. When no regularization is employed, the number of converged significant figures in the expectation values of such singular operators is roughly half (or even less) of the number of converged figures in the expectation values of operators representing global quantities.

In table 1, we show the computed expectation values of $H_{\mathrm{MV}}, \delta\left(\mathbf{r}_{i}\right)$, and $\delta\left(\mathbf{r}_{i j}\right)$ for three arbitrarily selected states, ( $1 s^{2} n p^{1}$ with $n=2,7,12$ ), along with the highly accurate results of Wang et al [28] obtained for the lowest of these states. In this and other tables, as well as in the text, the tilde sign over an operator indicates that the regularization approach was used in the calculation of the expectation value. Let us take a closer look at the results shown in the table. For example, in the expectation value $\left\langle\tilde{H}_{\mathrm{MV}}\right\rangle$, six significant figures are converged, while in the expectation value $\left\langle H_{\mathrm{MV}}\right\rangle$ the number of converged figures is only four (or even three), in spite of using a very large basis set. The improvement is even more noticeable for the expectation values of the delta functions. The numbers of converged significant figures in the expectation values $\left\langle\tilde{\delta}\left(\mathbf{r}_{i}\right)\right\rangle$ and $\left\langle\tilde{\delta}\left(\mathbf{r}_{i j}\right)\right\rangle$ are ten and nine, respectively, while for $\left\langle\delta\left(\mathbf{r}_{i j}\right)\right\rangle$ and $\left\langle\delta\left(\mathbf{r}_{i j}\right)\right\rangle$, only five significant figures are converged. Similar behavior can be expected for the expectation values of more excited states. For example, in the case of the $1 s^{2} 12 p^{1}$ state, the highest considered in this work, $\left\langle\tilde{H}_{\mathrm{MV}}\right\rangle$ is converged to six significant figures.

A comparison of the converged significant figures of the calculated expectation values for the ground and excited states reveals two interesting points about the calculations. First, the results show that the regularization technique employed in this work very effectively increases the convergence rate of the expectation values of singular operators, even for highlyexcited states. Second, the number of basis functions used in the excited-state calculations suffices to obtain accurate expectation values, although it is clear that larger basis sets are required to compute the $\left\langle\tilde{\delta}\left(\mathbf{r}_{i}\right)\right\rangle$ and $\left\langle\tilde{\delta}\left(\mathbf{r}_{i j}\right)\right\rangle$ expectation values more accurately.

In table 2, we show the nonrelativistic total energy, $E_{\mathrm{nr}}$, which is the total energy including the leading relativistic, QED, and HQED corrections, $E_{\text {tot }}$, and some other key expectation values obtained for the lowest eleven ${ }^{2} P$ states of the lithium atom. The expectation values include the mass-velocity correction $\left\langle\tilde{H}_{\mathrm{MV}}\right\rangle$, the Dirac delta functions $\langle\tilde{\delta}(\mathbf{r})\rangle$, the orbit-orbit correction $\left\langle H_{\mathrm{OO}}\right\rangle$, and the Araki-Sucher distribution $\left\langle\mathcal{P}\left(1 / r_{i j}^{3}\right)\right\rangle$.

The nonrelativistic energies of the lowest $1 s^{2} 2 p^{1}$ state and some of the higher excited states $\left(1 s^{2} n p^{1} n=4, \ldots, 10\right)$ can be compared with the values reported by Wang et al [28, 29]. For the $1 s^{2} 2 p^{1}$ state, the value obtained in a basis of 33600 Hy functions and then extrapolated to an infinite number of functions is -7.41015653265241 (3) hartree. Our energy of -7.41015653263 hartree obtained in the present work using only 9000 ECG basis functions agrees with that value to 11 decimal figures and lies slightly higher. Also, for the same number of basis functions, the computed nonrelativistic energies in this work are nearly as accurate as their results. For instance, the -7.410156532647379 hartree value for the

Table 4. $2^{2} P \leftarrow n^{2} P$ transition energies of ${ }^{6} \mathrm{Li}$ and ${ }^{7} \mathrm{Li}$ computed using the infinite-nuclear-mass (i) nonrelativistic energies and then gradually corrected by including finite-nuclear-mass effects ( f ), relativistic corrections, and the QED and HQED corrections. As the QED and HQED Hamiltonians are only valid for an infinite nuclear mass, the corresponding energy corrections are computed using the wave functions obtained in infinite nuclear mass calculations. All values are in $\mathrm{cm}^{-1}$.

${ }^{\text {a }}$ The reported values are for the naturally occurring mixture of ${ }^{6} \mathrm{Li}$ and ${ }^{7} \mathrm{Li}$ isotopes.
${ }^{\mathrm{b}}$ Values of $14903.520341(41) \mathrm{cm}^{-1}$ are used for the gravity centers of $2^{2} P_{1 / 2}$ and $2^{2} P_{3 / 2}$ with energies of $14903.296792(23)$ and $14903.632116(18) \mathrm{cm}^{-1} \mathrm{in}$ the transition energy calculations.
${ }^{\text {c }}$ The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ with energies of $16021.7796(10)$ and $16021.8760(10) \mathrm{cm}^{-1}$, respectively.
${ }^{\mathrm{d}}$ The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ with energies of $21565.9291(15)$ and $21565.9692(15) \mathrm{cm}^{-1}$, respectively.
${ }^{\text {e}}$ The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ with energies of $24111.8471(20)$ and $24111.8681(20) \mathrm{cm}^{-1}$, respectively.
${ }^{\mathrm{f}}$ The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ with energies of $25487.4142(100)$ and $25487.4262(100) \mathrm{cm}^{-1}$, respectively.
${ }^{g}$ Values of $14903.871689(41) \mathrm{cm}^{-1}$ are used for the gravity centers of $2^{2} P_{1 / 2}$ and $2^{2} P_{3 / 2}$ with energies of $14903.648130(23)$ and $14903.983468(18) \mathrm{cm}^{-1}$ in the transition energy calculations.
${ }^{\mathrm{h}}$ The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ with energies of $16021.904870(10)$ and $16022.001270(10) \mathrm{cm}^{-1}$, respectively.
${ }^{\text {i }}$ The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ with energies of $21566.106070(15)$ and $21566.146170(15) \mathrm{cm}^{-1}$, respectively.
${ }^{\text {j }}$ The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ with energies of $24112.050670(20)$ and $24112.071770(20) \mathrm{cm}^{-1}$, respectively.
${ }^{\mathrm{k}}$ The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ with energies of $25487.634870(100)$ and $25487.646870(100) \mathrm{cm}^{-1}$, respectively.
total infinite-nuclear-mass energy computed by Wang et al [26] using 9170 basis functions and the -7.41015653263 hartree value obtained in this work using 9000 ECG basis functions have errors of nearly the same magnitude when compared to the more accurate extrapolated result.

In order to evaluate the efficiency of the ECG basis, additional calculations are performed for the lowest ${ }^{2} P$ state. They involved gradually increasing the number of basis func-
tions from 10000 to 13500 ECGs for ${ }^{7} \mathrm{Li}$ and calculating the nonrelativistic energies of ${ }^{6} \mathrm{Li}$ and ${ }^{\infty} \mathrm{Li}$. Table 3 shows the energies obtained from these calculations. As expected, when the basis size increases, the energy continues to decrease. We estimate that, if we had the capability to include $30000+$ ECG basis functions in our basis set and optimize them thoroughly, the convergence of the energy would have been similar to that achieved by Wang et al using Hy-type


Figure 1. The difference ( $\Delta E=\Delta E_{\text {Calculated }}-\Delta E_{\text {Experimental }}$ ) between the transition energies computed in this work and experimental transitions. For both isotopes, the $2^{2} P \leftarrow n^{2} P, n=2, \ldots, 6$ experimental transition energies are taken from reference [55]. The experimental transition energies, of $2^{2} P \leftarrow n^{2} P, n=8, \ldots, 12$ of ${ }^{7} \mathrm{Li}$ are taken from references [57,58]. The calculated transition energies are taken from table 4. The small error bars at the top of each column represent estimated uncertainties in the experimental data. The gravity centers of ${ }^{2} P_{1 / 2}$ and ${ }^{2} P_{3 / 2}$ have been used for all states.
basis functions. However, this would have required an quantity of computational resources that would have exceeded the amount we were able to allocate for this work. The convergence of the energies in table 3 also demonstrates the importance of optimizing the nonlinear variational parameters of the Gaussian functions. In table 2, we show the energies obtained from our calculations along with the values reported by Wang et al in [29]. The values obtained in this work for higher states using more compact wave functions are nearly as accurate as those reported in reference [29], where large Hy-type basis sets of up to 22302 terms were employed.

Table 4 presents transition energy values calculated using the infinite-nuclear-mass and finite-nuclear-mass nonrelativistic energies, and with energies that include the relativistic, QED, and HQED corrections. The transition energies are calculated with respect to the $1 s^{2} 2 p^{1}$ state. In addition to the calculated values, some of the relevant experimental results are also shown in the table. These include the measurements of the 31 lowest ${ }^{2} P$ states reported by France back in 1930 [54] and the results taken from the following more recent experimental works. We start with the 1959 work of Johansson [56]; in that work, Johansson made some refinements to the energies reported by France. In 1995, Radziemski et al [55] made further improvements and reported the transition energies of the ${ }^{6} \mathrm{Li}$ and ${ }^{7} \mathrm{Li}$ isotopes. In 2010, Oxley and Collins [57,58] reported very accurate measurements of eight ${ }^{2} P$ states $\left(1 s^{2} n p^{1}, n=8, \ldots, 15\right)$ of the ${ }^{7} \mathrm{Li}$ isotope.

The following observations can be made upon examining the results, including experimental and theoretical data, presented in table 4:

- The transition energies for the lower states reported by Johansson [56], Radziemski et al [55], and Oxley and Collins [57,58] are relatively close to each other. However, the differences between the measured values are larger than the reported uncertainties. Also, the differences between the values reported by France [54] and the values from more recent papers [55-58] are relatively large (about $0.25 \mathrm{~cm}^{-1}$ ). The results of the four former studies [55-58] are more compatible with each other, thus, as it seems, more reliable, and they are used for comparison with the calculated transition energies in the present work.
- As one can see in the table, the differences between the experimental and nonrelativistic infinite-nuclear-mass computed transition energies ( $\mathrm{nr}(\mathrm{i})$ ) are relatively large and range from 0.5 to $1.25 \mathrm{~cm}^{-1}$. A significant improvement to the results is obtained when the finite mass of the nucleus replaces the infinite mass in the calculations. The replacement causes the difference between the calculated and experimental values to decrease significantly and to range between -0.3 and $0.3 \mathrm{~cm}^{-1}$.
- For ${ }^{6} \mathrm{Li}$, the only available quality experimental data were reported by Radziemski et al [55]. The differences between the calculated transition energies obtained using $E_{\mathrm{nr}}$ and the experimental values are relatively large and range from 0.2 to $0.3 \mathrm{~cm}^{-1}$. With the inclusion of the relativistic, QED, and HQED corrections, the differences decrease to $0.045,0.011$, and $0.011 \mathrm{~cm}^{-1}$, respectively. The comparison between the calculated and experimental values is shown in figure 1 .

Table 5. Isotope transition-energy shifts of ${ }^{6} \mathrm{Li}$ with respect to ${ }^{7} \mathrm{Li}$. All values are given in $\mathrm{cm}^{-1}$.

| Transition | Basis | (nr) | ( $\mathrm{nr}+\mathrm{rel}$ ) | Exp. [55] |
| :---: | :---: | :---: | :---: | :---: |
| $2^{2} P \leftarrow 3^{2} P$ | $\begin{aligned} & 6000 \\ & 7000 \\ & 8000 \\ & 9000 \end{aligned}$ | $\begin{aligned} & -0.1252030 \\ & -0.1252030 \\ & -0.1252030 \\ & -0.1252030(1) \end{aligned}$ | $\begin{aligned} & -0.1252333 \\ & -0.1252334 \\ & -0.1252334 \\ & -0.1252334(1) \end{aligned}$ | -0.1253(10) |
| $2^{2} P \leftarrow 44^{2} P$ | $\begin{gathered} 7000 \\ 8000 \\ 9000 \\ 10000 \end{gathered}$ | $\begin{aligned} & -0.1758085 \\ & -0.1758086 \\ & -0.1758086 \\ & -0.1758086(1) \end{aligned}$ | $\begin{aligned} & -0.1758461 \\ & -0.1758462 \\ & -0.1758462 \\ & -0.1758462(1) \end{aligned}$ | -0.1770(30) |
| $2^{2} P \leftarrow 55^{2} P$ | $\begin{gathered} 7000 \\ 8000 \\ 9000 \\ 10000 \end{gathered}$ | $\begin{aligned} & -0.2011964 \\ & -0.2011965 \\ & -0.2011965 \\ & -0.2011965(1) \end{aligned}$ | $\begin{aligned} & -0.2012366 \\ & -0.2012366 \\ & -0.2012366 \\ & -0.2012366(1) \end{aligned}$ | -0.2036(40) |
| $2^{2} P \leftarrow 66^{2} P$ | $\begin{gathered} 8000 \\ 9000 \\ 10000 \\ 11000 \end{gathered}$ | $\begin{aligned} & -0.2156708 \\ & -0.2156708 \\ & -0.2156708 \\ & -0.2156709(1) \end{aligned}$ | $\begin{aligned} & -0.2157121 \\ & -0.2157121 \\ & -0.2157121 \\ & -0.2157121(1) \end{aligned}$ | $-0.2207(200)$ |
| $2^{2} P \leftarrow 7^{2} P$ | $\begin{gathered} 9000 \\ 10000 \\ 11000 \\ 12000 \end{gathered}$ | $\begin{aligned} & -0.2246817 \\ & -0.2246819 \\ & -0.2246820 \\ & -0.2246820(1) \end{aligned}$ | $\begin{aligned} & -0.2247233 \\ & -0.2247237 \\ & -0.2247238 \\ & -0.2247239(1) \end{aligned}$ |  |
| $2{ }^{2} P \leftarrow 8^{2} P$ | $\begin{aligned} & 11000 \\ & 12000 \\ & 13000 \\ & 14000 \end{aligned}$ | $\begin{aligned} & -0.2306645 \\ & -0.2306645 \\ & -0.2306646 \\ & -0.2306647(1) \end{aligned}$ | $\begin{aligned} & -0.2307063 \\ & -0.2307063 \\ & -0.2307065 \\ & -0.2307068(2) \end{aligned}$ |  |
| $2{ }^{2} P \leftarrow 9^{2} P$ | $\begin{aligned} & 12000 \\ & 13000 \\ & 14000 \\ & 15000 \end{aligned}$ | $\begin{gathered} -0.2348361 \\ -0.2348361 \\ -0.2348361 \\ -0.2348362(1) \end{gathered}$ | $\begin{gathered} -0.2348780 \\ -0.2348781 \\ -0.2348781 \\ -0.2348782(1) \end{gathered}$ |  |
| $2{ }^{2} P \leftarrow 10^{2} P$ | $\begin{aligned} & 13000 \\ & 14000 \\ & 15000 \\ & 16000 \end{aligned}$ | $\begin{aligned} & -0.2378592 \\ & -0.2378592 \\ & -0.2378593 \\ & -0.2378593(1) \end{aligned}$ | $\begin{aligned} & -0.2379012 \\ & -0.2379015 \\ & -0.2379015 \\ & -0.2379016(1) \end{aligned}$ |  |
| $2{ }^{2} P \leftarrow 11^{2} P$ | $\begin{aligned} & 13000 \\ & 14000 \\ & 15000 \\ & 16000 \end{aligned}$ | $\begin{aligned} & -0.2401193 \\ & -0.2401192 \\ & -0.2401193 \\ & -0.2401194(1) \end{aligned}$ | $\begin{aligned} & -0.2401615 \\ & -0.2401618 \\ & -0.2401619 \\ & -0.2401619(1) \end{aligned}$ |  |
| $2^{2} P \leftarrow 12^{2} P$ | $\begin{aligned} & 13000 \\ & 14000 \\ & 15000 \\ & 16000 \end{aligned}$ | $\begin{aligned} & -0.2418518 \\ & -0.2418522 \\ & -0.2418523 \\ & -0.2418525(1) \end{aligned}$ | $\begin{aligned} & -0.2418942 \\ & -0.2418950 \\ & -0.2418951 \\ & -0.2418952(1) \end{aligned}$ |  |

- In the case of the less energetic states of ${ }^{7} \mathrm{Li}$, there have been four experimental reports [55-58]. For the less excited states, the values reported by Johansson [56] and

Radziemski et al [55] are in full agreement with each other and with the computed values obtained in this work. The calculated differences are very similar to those of


Figure 2. Isotope transition-energy shifts of ${ }^{6} \mathrm{Li}$ with respect to ${ }^{7} \mathrm{Li}$. The $(\mathrm{nr}(\mathrm{f})+\mathrm{rel}(\mathrm{f}))$ transition values have been used in the isotope shift calculations. All values are given in $\mathrm{cm}^{-1}$. The experimental isotope shifts are taken from reference [55].
${ }^{6} \mathrm{Li}$. The inclusion of the relativistic, QED, and HQED corrections significantly improves the agreement with the experimental data and the differences decrease to less than $0.03 \mathrm{~cm}^{-1}$. For the more excited states, the only available values are those reported by Oxley and Collins [57, 58]. Because the two former works [55, 56] have no data in common with the two latter ones, it is not possible to compare the accuracy of the reported data. However, the differences between the transition energies computed in this work and the values reported by Oxley and Collins show a trend that seems contradictory in comparison to the previous papers. For example, the differences between the calculated transition energies using $E_{\mathrm{nr}}$ and the experimental values are relatively small (less than $0.09 \mathrm{~cm}^{-1}$ ). At the same time, inclusion of the relativistic, QED, and HQED corrections significantly increases the differences. Based on the calculated transitions in the present work and on the comparison made above, we believe that the actual uncertainties in the measured values are likely to be larger than the reported uncertainties (see table 4 and figure 1).

- It is worth mentioning that the main sources of error in calculating the transition energies are the QED and HQED corrections. To calculate the QED term, a single approximate value for the Bethe logarithm $\left(\ln k_{0}\right)$ is used for all states. This is certainly an approximation. We estimate that the use of a more accurate logarithm value could change the transition energies listed in table 4 by about $0.008 \mathrm{~cm}^{-1}$. The second reason for the error arises from the approximate form of the expression used to compute the HQED expectation value. Here, we roughly estimate that the computed transition energies could change by about $0.0007 \mathrm{~cm}^{-1}$ when more accurate HQED correction values become available.

Table 5 shows the isotope shifts in the transition energies determined from the results of our calculations. The experimental data [55] are shown for comparison. In determining the shift values, the non-relativistic ( nr ) and relativistic corrected ( $\mathrm{nr}+$ rel) frequencies are used. Comparing the computed and experimental values reveals two key points. First, the computed values, $(\mathrm{nr})$ and $(\mathrm{nr}+\mathrm{rel})$, are in full agreement with the experimental values and they are within the uncertainties of the experimental data. Second, the results show that the finite nuclear mass effect is small for less energetic states, but it increases with the excitation level. For instance, the frequency shifts for the lowest transition $\left(2^{2} P \leftarrow 3{ }^{2} P\right)$ are $0.1252030 \mathrm{~cm}^{-1}(\mathrm{nr})$ and $-0.1252334 \mathrm{~cm}^{-1}(\mathrm{nr}+$ rel $)$ while the corresponding values for the $2{ }^{2} P \leftarrow 12{ }^{2} P$ transition are -0.2418518 and $-0.2418952 \mathrm{~cm}^{-1}$, respectively. This is an almost two-fold increase (figure 2).

Finally, in table 6, we show the calculated expectation values of some powers of the inter-particle distances. As expected, both the average nucleus-electron and elec-tron-electron distances increase rapidly with the increasing principal quantum number. It is worth mentioning that the distances differ slightly between the ${ }^{6} \mathrm{Li}$ and ${ }^{7} \mathrm{Li}$ isotopes. The difference originates from the different reduced masses of the electron used in the calculations of the two isotopes. For instance, for the most excited state, the $\left\langle r_{\mathrm{ne}}\right\rangle$ values for the ${ }^{6} \mathrm{Li}$ and ${ }^{7} \mathrm{Li}$ isotopes are 71.4940 and 71.4934 a.u., respectively. The corresponding values for $\left\langle r_{\mathrm{ee}}\right\rangle$ are 142.512 and 142.511 a.u., respectively.

## 4. Summary

The lowest eleven states of the ${ }^{2} P$ series $\left(1 s^{2} n p^{1}, n=\right.$ $2, \ldots, 12$ ) of the lithium atom were studied using very accurate variational calculations employing explicitly correlated all-electron Gaussian functions. The calculations yielded

Table 6. Expectation values, $\left\langle r_{i}^{p}\right\rangle$ and $\left\langle r_{i j}^{p}\right\rangle(p=-2, \ldots, 2)$ evaluated with the largest basis set generated for each state in this work. All values are in atomic units.

| State | Isotope | $\left\langle r_{\text {ne }}^{-2}\right\rangle$ | $\left\langle r_{\text {ee }}^{-2}\right\rangle$ | $\left\langle r_{\text {ne }}^{-1}\right\rangle$ | $\left\langle r_{\text {ee }}^{-1}\right\rangle$ | $\left\langle r_{\text {ne }}\right\rangle$ | $\left\langle r_{\text {ee }}\right\rangle$ | $\left\langle r_{\text {ne }}^{2}\right\rangle$ | $\left\langle r_{\text {ee }}^{2}\right\rangle$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $1 s^{2} 2 p^{1}$ | ${ }^{6} \mathrm{Li}$ | $9.96514485(0)$ | $1.42164231(0)$ | $1.87946358(0)$ | $0.698751993(0)$ | $1.95723729(0)$ | 3.470879 40(0) | $9.31711136(0)$ | $18.6851758(0)$ |
|  | ${ }^{7} \mathrm{Li}$ | $9.96540948(0)$ | $1.42167509(0)$ | $1.87948808(0)$ | $0.698759070(0)$ | $1.95722074(0)$ | $3.47085327(0)$ | $9.31696402(0)$ | $18.6848879(0)$ |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.96699963(0)$ | $1.42187207(0)$ | $1.87963532(0)$ | $0.698801595(0)$ | $1.95712125(0)$ | $3.47069624(0)$ | $9.31607855(0)$ | $18.6831580(0)$ |
| $1 s^{2} 3 p^{1}$ | ${ }^{6} \mathrm{Li}$ | $9.95406339(0)$ | $1.37819289(0)$ | $1.83018692(0)$ | 0.599589241 (0) | $4.40897109(0)$ | $8.35499208(0)$ | 56.508 6959(0) | 113.045 290(0) |
|  | ${ }^{7} \mathrm{Li}$ | $9.95432722(0)$ | $1.37822513(0)$ | $1.83021115(0)$ | 0.599595889 (0) | $4.40892701(0)$ | $8.35491105(0)$ | 56.507 5879(0) | $113.043082(0)$ |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.95591257(0)$ | $1.37841887(0)$ | $1.83035677(0)$ | $0.599635838(0)$ | $4.40866213(0)$ | $8.35442407(0)$ | $56.5009292(0)$ | $113.029812(0)$ |
| $1 s^{2} 4 p^{1}$ | ${ }^{6} \mathrm{Li}$ | $9.95160312(0)$ | 1.367877 21(0) | $1.81320064(0)$ | $0.565471099(0)$ | $7.86184137(0)$ | $15.2545513(1)$ | $190.909314(0)$ | $381.839008(0)$ |
|  | ${ }^{7} \mathrm{Li}$ | $9.95186677(0)$ | $1.36790930(0)$ | $1.81322475(0)$ | 0.565477 510(0) | $7.86175685(0)$ | $15.2543894(1)$ | $190.905244(0)$ | 381.830876 (0) |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.95345102(0)$ | 1.368102 12(0) | $1.81336958(0)$ | $0.565516032(0)$ | $7.86124896(0)$ | $15.2534164(1)$ | 190.880786 (0) | 381.782 009(0) |
| $1 s^{2} 5 p^{1}$ | ${ }^{6} \mathrm{Li}$ | $9.95075907(0)$ | $1.36425681(0)$ | $1.80541642(0)$ | $0.549851804(0)$ | $12.3149846(0)$ | 24.158 1252(1) | 481.587 170(1) | 963.191 380(2) |
|  | ${ }^{7} \mathrm{Li}$ | $9.95102266(0)$ | $1.36428884(0)$ | $1.80544045(0)$ | $0.549858084(0)$ | $12.3148467(0)$ | 24.1578564 (1) | $481.576430(1)$ | 963.169 908(2) |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.95260654(0)$ | $1.36448132(0)$ | $1.80558487(0)$ | $0.549895819(0)$ | $12.3140177(0)$ | $24.1562414(1)$ | 481.511 890(1) | $963.040879(2)$ |
| $1 s^{2} 6 p^{1}$ | ${ }^{6} \mathrm{Li}$ | $9.95039328(0)$ | $1.36267111(0)$ | $1.80121580(0)$ | $0.541428381(0)$ | $17.7682712(0)$ | 35.063 2747(1) | 1017.61491(0) | 2035.24510 (2) |
|  | ${ }^{7} \mathrm{Li}$ | $9.95065684(0)$ | $1.36270311(0)$ | $1.80123979(0)$ | $0.541434582(0)$ | $17.7680669(0)$ | 35.062 8733(1) | 1017.591 58(0) | 2035.19844 (2) |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.95224055(0)$ | $1.36289542(0)$ | $1.80138396(0)$ | $0.541471846(0)$ | $17.7668395(0)$ | 35.0604612(1) | $1017.45134(0)$ | $2034.91802(2)$ |
| $1 s^{2} 7 p^{1}$ | ${ }^{6} \mathrm{Li}$ | 9.95020946 (2) | $1.36186962(3)$ | $1.79869471(0)$ | $0.536375011(0)$ | $24.2216686(3)$ | 47.9692316 (5) | 1908.069 00(5) | 3816.1522(1) |
|  | ${ }^{7} \mathrm{Li}$ | $9.95047300(2)$ | $1.36190161(3)$ | $1.79871867(0)$ | $0.536381163(0)$ | $24.2213853(3)$ | $47.9686721(5)$ | 1908.02442 (5) | 3816.0631(1) |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.95205664(2)$ | $1.36209384(3)$ | $1.79886269(0)$ | $0.536418124(0)$ | $24.2196828(3)$ | 47.965 3099(5) | $1907.75652(5)$ | 3815.5273(1) |
| $1 s^{2} 8 p^{1}$ | ${ }^{6} \mathrm{Li}$ | 9.95010706 (6) | $1.3614217(1)$ | $1.79706404(0)$ | $0.533107428(0)$ | 31.675 167(6) | 62.87596 (1) | 3282.030(1) | 6564.073(2) |
|  | ${ }^{7} \mathrm{Li}$ | 9.950370 59(6) | 1.361 4537(1) | 1.797087 99(0) | $0.533113545(0)$ | $31.674793(6)$ | 62.87495(1) | 3281.952(1) | 6563.918(2) |
|  | ${ }^{\infty} \mathrm{Li}$ | 9.95195418 (6) | 1.361 6457(1) | $1.79723189(0)$ | $0.533150299(0)$ | 31.672 545(6) | 62.870 50(1) | 3281.486(1) | 6562.986(2) |
| $1 s^{2} 9 p^{1}$ | ${ }^{6} \mathrm{Li}$ | $9.9500454(1)$ | 1.361 1524(9) | $1.79594901(0)$ | 0.530873610 (3) | $40.12878(4)$ | 79.782 55(5) | 5288.59(1) | 10 577.19(3) |
|  | ${ }^{7} \mathrm{Li}$ | 9.9503090 (1) | 1.361 1844(9) | 1.795972 94(0) | 0.530879700 (3) | 40.12831(4) | 79.781 62(5) | 5288.46(1) | 10576.94 (3) |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.9518925(1)$ | $1.3613766(9)$ | $1.79611676(0)$ | 0.530916290 (3) | 40.125 48(4) | 79.77600 (5) | 5287.71(1) | 10575.44(3) |
| $1 s^{2} 10 p^{1}$ | ${ }^{6} \mathrm{Li}$ | $9.9500062(2)$ | 1.360 9802(1) | $1.79515310(0)$ | $0.529279407(3)$ | 49.582 48(4) | 98.689 71(6) | 8096.83(1) | 16 193.67(3) |
|  | ${ }^{7} \mathrm{Li}$ | 9.950 2697(2) | $1.3610122(1)$ | $1.79517702(0)$ | $0.529285465(3)$ | $49.58194(4)$ | 98.688 63(6) | 8096.65(1) | 16193.31 (3) |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.9518533(2)$ | 1.361 2043(1) | $1.79532075(0)$ | $0.529321865(3)$ | 49.578 68(4) | 98.682 16(6) | 8095.55(1) | 16191.11 (3) |

Table 6. Continue

| $1 s^{2} 11 p^{1}$ | ${ }^{6} \mathrm{Li}$ | 9.949 9792(3) | $1.3608658(1)$ | $1.79456523(0)$ | $0.528102077(8)$ | 60.0368(2) | 119.5982(5) | 11896.10(9) | $23792.2(2)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | ${ }^{7} \mathrm{Li}$ | 9.9502428 (3) | $1.3608978(1)$ | 1.794589 12(0) | $0.528108084(8)$ | 60.0363(2) | 119.5973(5) | 11895.88(9) | $23791.8(2)$ |
|  | ${ }^{\infty} \mathrm{Li}$ | 9.9518263 (3) | $1.3610898(1)$ | 1.79473270 (0) | $0.528144176(8)$ | 60.0334(2) | 119.5914(5) | 11894.55(9) | 23789.1(2) |
| $1 s^{2} 12 p^{1}$ | ${ }^{6} \mathrm{Li}$ | 9.949 9583(9) | $1.3607872(2)$ | 1.79411871 (1) | $0.527207942(9)$ | 71.4940(8) | 142.512(2) | 16896.6(4) | $33793.2(9)$ |
|  | ${ }^{7} \mathrm{Li}$ | $9.9502219(9)$ | $1.3608192(2)$ | $1.79414260(1)$ | 0.527213941 (9) | 71.4934(8) | 142.511(2) | 16896.3(4) | 33792.6 (9) |
|  | ${ }^{\infty} \mathrm{Li}$ | $9.9518054(9)$ | $1.3610112(2)$ | $1.79428615(1)$ | 0.527249 985(9) | 71.4899(8) | 142.504(2) | 16894.4(4) | 33788.8 (9) |

nonrelativistic total energies and the corresponding wave functions for the considered states. The wave functions were used in perturbation-theory calculations of the leading relativistic and QED corrections to the energies of the considered states. The transition energies for the states determined with respect to the lowest $1 s^{2} 2 p^{1}$ state were also calculated. The transition energies were compared with the experimental values. The transition energies obtained using the nonrelativistic energies of the states differed from the most accurate experimental results by less than $0.3 \mathrm{~cm}^{-1}$. The inclusion of the relativistic, QED, and HQED corrections reduced the difference to less than $0.1 \mathrm{~cm}^{-1}$. The transition frequencies determined for ${ }^{6} \mathrm{Li}$ and ${ }^{7} \mathrm{Li}$ were used to calculate the isotopic shifts. The calculated shifts agreed with the available experimental results within the reported experimental uncertainties.

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## Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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