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Using Koopmans' theorem for constructing basis sets: approaching high Rydberg excited states of lithium with a compact Gaussian basis†

Jan Šmydke 

For accurate *ab initio* description of Rydberg excited states, this study suggests generating appropriate diffuse basis functions by cheap variational optimization of virtual orbitals of the corresponding ion core. By following this approach, dozens of converged correlated lithium Rydberg states, namely, all the states up to $24\ ^2S$, $25\ ^2P$, $14\ ^2D$, $16\ ^2F$ and $16\ ^2G$, not yet achieved *via* other *ab initio* approaches, could be obtained at the EOM-CCSD level of theory with compact and mostly state-selective contracted Gaussian basis sets. Despite its small size and Gaussian character, the optimized basis leads to highly accurate excitation energies that differ merely in the order of meV from the reference state-of-the-art explicitly correlated Gaussian method and even surpass Full-CI results on the Slater basis by an order of magnitude.

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1 Introduction

Investigation of Rydberg excited states of atomic and molecular systems is mostly the domain of the quantum defect theory (QDT),¹ in which a motion of the highly excited electron is modeled by an effective one-electron approach. It is assumed that the average distance between the highly excited electron and the positively charged ion core is sufficiently large that the electron experiences a Coulombic field of the ion core analogous to the field in the hydrogen atom, though effectively shielded by the other electrons. The energy spectrum of such a model necessarily differs from the spectrum of hydrogen, introducing characteristic quantum defects δ of the principal quantum number n in the energy level formula

$$E_n = -\frac{\text{Ry}}{(n - \delta)^2} \quad (1)$$

where Ry stands for the Rydberg constant. By providing accurate quantum defects of a system (*e.g.*, from experimental transitions), the asymptotic wave functions can be expressed analytically and the properties further evaluated. Although the QDT proved to be robust and capable, it represents a one-electron approach, not an *ab initio* theory, and depends on the externally supplied energy spectrum. Its applicability is also

limited to rather highly excited states, in which the true Rydberg character of the system is sufficiently retained.

By contrast, the *ab initio* theories for excited states either suffer from overall poor accuracy of the computed energy spectrum or provide only the few lowest excited states in high precision. This stems from the inherent complexity of the *ab initio* methods, which deal with many-body systems and balance between scalability and an accurate description of the electronic correlation. Nevertheless, the need for a proper *ab initio* description of the Rydberg states as opposed to the quantum defect asymptotic theory comes also hand in hand with the fact that the Rydberg states often interact with valence excited states in a similar energy window, strongly affecting the spectroscopy and dynamics of the underlying chemical systems.² In such cases, an efficient full many-body treatment is thus necessary.

The sharp contrast between the ability of the advanced quantum chemical methods to describe highly correlated ground electronic states even in difficult electronic structures on the one hand and their failure to reliably describe the higher excited states on the other hand grows out of the insufficiency of the commonly used basis sets to reach and mimic the diffuse and structurally more complicated excited state wave functions. The standard Gaussian basis sets (GTO) tend to be extensively optimized for the ground state to describe enough electronic correlation while keeping the number of basis functions low. The exponential-type basis functions (ETO) like the Slater-type orbitals (STO) and Coulomb–Sturmians (CS) are, of course, of higher quality than the Gaussians due to the correct cusp at nuclei and their natural diffuse characteristics. Despite the

Department of Radiation and Chemical Physics, FZU - Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 18200 Praha 8, Czech Republic.
E-mail: jan.smydke@gmail.com

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superiority of the ETOs and in particular of the CS functions, which constitute a complete orthogonal set, the ETOs (as well as the GTOs) are by no other means optimal for excited state description of many-electron systems.

Hence, a common way of building custom basis sets for excited states is to extend a standard GTO basis with a large set of primitive diffuse functions. The primitives are often put in the form of the even tempered Gaussians (ETG), in which the exponents are given by a simple formula

$$\log \zeta_k = \log \zeta_0 + k \log \alpha; \quad \log \alpha < 0, k = 0 \dots (N - 1) \quad (2)$$

where ζ_0 and α are the ETG series parameters and N is the size of the set. Such a series can provide many diffuse functions with just a few variable parameters. However, the drawback of adding extra functions to a basis is that they tend to cause near linear dependencies, leading to serious numerical issues. A disadvantage of the ETG sets is that they do not consistently cover a larger portion of the spectrum and are hardly applicable to problems with excessive demands on precision and flexibility like in dynamical studies of electronic resonances under complex scaled representation.³ By extending a basis with extra diffuse functions, it is practically sufficient that the resulting set is not linearly dependent and satisfactorily describes a particular feature of interest.

The aim of the present study is a tailored optimization of the diffuse basis rather than a mere inclusion of a large number of functions. The intention is to systematically generate such a basis that would approximate at least a few Rydberg orbitals. Such orbitals could then serve as the optimal functions for a correlated treatment of the corresponding Rydberg states. The ultimate outcome, although beyond the scope of this work, might lead to a specific diffuse basis suitable for a complex scaling treatment of related resonance states, which is highly sensitive to the basis set quality.³ In order to employ standard quantum chemistry codes, this study exclusively uses Gaussian basis sets. Nevertheless, the investigated approach is universal and applicable to any basis set type.

This study focuses on systems that can be modeled as a closed-shell ion core with an odd electron moving around. For such systems, a simple trick can be used to describe the Rydberg orbitals that can be the target of the basis set optimization. As is well known from Koopmans' theorem,⁴ the canonical restricted Hartree–Fock (RHF) virtual orbitals describe an electron captured by the system (*i.e.* the Rydberg electron captured by the ion core). Since the eigenvalues of the converged Fock operator (*i.e.* the one defined by the converged Hartree–Fock occupied orbitals) are stationary with respect to variations of the eigenvectors, the Rydberg orbitals can be found by a variational procedure. For the lithium atom (Li), which is the subject of this work, it means that by a variational minimization of the Li^+ virtual orbital energies, while varying the basis set parameters and at the same time maintaining the Hartree–Fock energy minimal (in order to keep the converged Fock operator), one should end up with such Li^+ virtual orbitals that could serve as the appropriate basis functions for the

description of the Rydberg excited electron in the neutral Li atom.

In principle, the presented idea of variational minimization of virtual orbitals for obtaining the Rydberg functions is not confined to closed-shell ion cores but could be used with any system for which the Koopmans' theorem for electron affinity is valid. For open-shell ion cores, it is generally not correct to use the unrestricted (UHF) or an arbitrary restricted open-shell Hartree–Fock (ROHF) method variant. However, the canonical ROHF method as discussed by Plakhutin *et al.*^{5–8} guarantees the validity of Koopmans' theorem for various open shell electronic systems, so the presented method is applicable for them too.

Although the suggested approach is based on the Hartree–Fock model only, it can be anticipated that due to the Rydberg character of the excited electron, the model can be satisfactory at least for higher excited states. In our earlier studies of helium (He) resonances,^{3,9} we used an analogous approach to obtain a basis for He excited states by appropriately modifying the Fock operator¹⁰ so that the virtual orbitals describe excited electrons rather than the captured ones. The quality of the optimized basis was outstanding, leading not only to good transition energies but also to a wide interval of resonance energy stability along the complex scaling parameter θ . Such a basis enabled an extensive non-Hermitian dynamical propagation of He under extremely intense laser radiation.

We are not aware of many other approaches for specific Gaussian basis set optimization regarding the Rydberg states. Durand and Volatron¹¹ used electronically correlated transition energies computed using the configuration interaction method to find the optimal diffuse Gaussian exponents for the description of Rydberg states of water. Kaufmann *et al.*¹² provide a universal ready-to-use formula for Gaussian exponents to describe either the atomic Rydberg functions or the low-lying continuum states. They basically tried an approximate one-to-one mapping between exponential-type functions and Gaussians in order to cover a portion of a complete bound or continuum spectrum. Despite using a less sophisticated principal idea, the method introduced in the present study offers more flexibility in the description of specific systems as opposed to using a fixed universal basis and is also less limited as to the number of achievable Rydberg states.

The rest of the article is organized as follows. Section 2 describes the basis set optimization and other computational details. Section 3 discusses important properties of the optimized basis and compares the resulting Rydberg excitation energies to other highly accurate values known in the literature. A summary of the results and conclusions are drawn in Section 4.

2 Computational details

The whole basis set optimization process can be summarized in the following. First, a standard basis set is included for a good description of the electronic correlation. That should suffice for



the ground as well as for the Rydberg states since the part of the wave function, in which the correlation plays a role, is in all states spatially distributed similarly; only the Rydberg electron occupies distant areas where it does not significantly contribute to the dynamical electronic correlation. To describe the Rydberg electron attracted by a closed-shell ion core, diffuse functions are appended to the basis and the virtual orbital energies of the ion core are minimized. This is achieved by varying the diffuse functions while maintaining the optimal Hartree–Fock energy and avoiding near linear dependencies. In accord with Koopmans' theorem, such optimal virtual orbitals are just the Rydberg orbitals. Since their shape is controlled solely by the Hartree–Fock field of the ion core, it is advantageous to improve the field quality before the actual virtual orbital optimization by an additional high-exponent function to mimic the wave-function cusp. Eventually, contracted basis functions are formed from the optimal Rydberg orbitals using their expansion coefficients (LCAO) in the primitive diffuse basis. The final basis set for productive computations of the Rydberg states then consists of the standard basis together with the high-exponent function and appropriate subsets of the contracted optimized Rydberg functions as discussed in Section 3.1.

Practically, for lithium, the well established aug-ano-pVQZ¹³ basis of Neese and Valeev has been chosen as the standard basis set. To improve the Hartree–Fock wave function of the Li⁺ ion core, an additional ETG series of 19 high-exponent primitive S functions was used to minimize the Hartree–Fock energy. From the resulting 1S orbital, an auxiliary contracted function was formed, consisting of the ETG primitives only, which was used further instead of the high-exponent series. Independently for each angular momentum L ∈ {S,P,D,F,G}, a mostly diffuse ETG set of the given L was added to the basis and by varying its parameters, the energy of the first Li⁺ virtual orbital of that L symmetry was minimized. The orbital optimization led to ETG sets that spanned not only diffuse functions but also rather tight ones. The process thus had to avoid such parameters that caused linear dependence of the ETG functions with the aug-ano-pVQZ basis. The optimal ETG parameters were then fixed, and only the number (N) of the ETG primitive functions was further gradually increased until a satisfactorily large number of virtual orbital energies were no longer changing by more than 10⁻⁹ a.u. The numbers of ETG primitives reached 30 for S, 50 for P, 40 for D, 30 for F, and 25 for G ETG series. In the end, all the optimized virtual orbitals, namely, 25 S, 28 P, 22 D, 21 F and 14 G, were contracted in the diffuse ETG subspace and put together in a final huge basis denoted as [25S-28P-22D-21F-14G]. The basis set in this notation means that it contains the aug-ano-pVQZ plus the high-exponent contracted S function plus the given numbers of optimal contracted Rydberg functions.

During the basis set optimization process, the Hartree–Fock orbital energies were calculated using the MRCC^{14,15} program package, while the multidimensional minimization itself was driven by the mdoptcli¹⁶ utility, which uses procedures from the GNU Scientific Library (GSL).¹⁷ All the correlated computations using the coupled cluster (CCSD) and equation of motion

coupled cluster (EOM-CCSD) methods employed the GAMESS 2021 R1¹⁸ package, recompiled to allow a large number of primitive basis functions.

3 Results and discussion

3.1 Properties of the optimized basis

It was found that the [7S-6P-5D] subset of the huge [25S-28P-22D-21F-14G] basis exhibits already converged CCSD ionization potential (IP) with respect to the basis set size and similarly also all the Li bound state excitation energies computed at the EOM-CCSD level (up to the state 8 ²S). This is apparent in Table 1, which shows that by adding more of the optimized diffuse S, P or D functions (basis [10S-9P-8D]) or by including F and G functions (basis [7S-6P-5D-4F-3G]) to the [7S-6P-5D] basis, the IP as well as the excitation energy values were no longer affected. The IP value (5.3877 eV) was calculated as the difference between the CCSD energy of the Li⁺ cation and the neutral Li atom, underestimating the experimental¹⁹ value of 5.3917 eV by 4 meV. This is in accordance with the expectations as the CCSD method is not Full-CI equivalent in the description of the neutral 3-electron Li system. The [7S-6P-5D] basis can thus be considered as a minimal saturated set that can safely be extended to achieve higher Li Rydberg states.

It should be stressed that the obtained diffuse basis was optimized for Li Rydberg states and not for Li⁺, although it was the virtual orbitals of the cation that determined the Li Rydberg functions. Therefore, Li⁺ excited states are not converged with respect to the basis. This can be seen from Table 2, where the not yet converged Li⁺ states are described by the very same basis sets as the converged states of the neutral Li in Table 1.

As anticipated above, to achieve higher Li Rydberg states of a particular angular momentum L, just more of the optimized Rydberg functions of the given L can be added to the minimal [7S-6P-5D] basis (schematically as [7S-6P-5D + kL]), since the

Table 1 Comparison of correlated ground and bound state excitation energies of neutral doublet Li resulting from three contracted basis sets. The ground state 2 ²S energy (ROHF and CCSD) is given in a.u., while the excitation energies (EOM-CCSD) as well as the ionization potential (CCSD) are in eV

State	[7S-6P-5D]	[7S-6P-5D-4F-3G]	[10S-9P-8D]
2 ² S ROHF	-7.4327268276	-7.4327268276	-7.4327268280
2 ² S CCSD	-7.4744349730	-7.4744349759	-7.4744353492
IP CCSD	5.3877	5.3877	5.3877
2 ² P	1.8472	1.8472	1.8472
3 ² S	3.3704	3.3704	3.3704
3 ² P	3.8317	3.8317	3.8317
3 ² D	3.8754	3.8753	3.8754
4 ² S	4.3378	4.3378	4.3378
4 ² P	4.5186	4.5186	4.5186
4 ² D	4.5373	4.5373	4.5373
4 ² F		4.5379	
5 ² S	4.7456	4.7456	4.7456
5 ² P	4.8341	4.8341	4.8341
5 ² D	4.8437	4.8437	4.8437
5 ² F		4.8440	
5 ² G		4.8441	



Table 2 Comparison of correlated ground and excitation energies of singlet Li^+ resulting from three contracted basis sets. The ground state 1^1S energy (RHF and CCSD) is given in a.u., while the excitation energies (EOM-CCSD) are in eV

State	[7S-6P-5D]	[7S-6P-5D-4F-3G]	[10S-9P-8D]
1^1S RHF	-7.2364151179	-7.2364151179	-7.2364151179
1^1S CCSD	-7.2764420008	-7.2764420020	-7.2764423045
2^1S	60.8448	60.8448	60.8446
2^1P	62.2642	62.2642	62.2610
3^1S	69.2199	69.2199	69.2194
3^1D	69.7706	69.7706	69.7474
3^1P	69.8285	69.8285	69.8204
4^1S	72.0843	72.0843	72.0826
4^1D	72.3562	72.3561	72.3458
4^1P	72.3774	72.3774	72.3753

Table 3 Comparison of correlated ground and bound state excitation energies of a neutral doublet Li above the state 7^2S for three contracted [7S-6P-5D + kL, L = S] basis sets. The ground state 2^2S energy (ROHF and CCSD) is given in a.u., while the excitation energies (EOM-CCSD) as well as the ionization potential (CCSD) are in eV

State	[7S-6P-5D]	[16S-6P-5D]	[25S-6P-5D]
2^2S ROHF	-7.4327268276	-7.4327268280	-7.4327268280
2^2S CCSD	-7.4744349730	-7.4744349806	-7.4744349805
IP CCSD	5.3877	5.3877	5.3877
7^2P	5.1070	5.1070	5.1070
7^2D	5.1097	5.1097	5.1097
8^2S	5.1540	5.1540	5.1540
9^2S	5.2116	5.2116	5.2116
10^2S	5.2610	5.2610	5.2610
11^2S	5.2990	5.2990	5.2990
12^2S	5.3264	5.3264	5.3264
13^2S	5.3457	5.3457	5.3457
14^2S	5.3592	5.3592	5.3592
15^2S	5.3684	5.3684	5.3684
16^2S	5.3747	5.3747	5.3747
17^2S			5.3790

resulting correlated states are no longer affected by the functions of other L. Truly, Table 3 shows that by gradually increasing the number of Rydberg S functions included to the minimal basis, the correlated bound states remain intact, and only new ^2S states emerge as the basis grows. This, as well as a strong dominance of the EOM-CCSD R_1 operator amplitude²⁰ that excites to the appropriate Rydberg orbital, confirms the Rydberg character of the states (*i.e.* systems of an electron and a net positive charge of the ion core, ignoring the interactions between that electron and the individual other electrons of the ion core) and hence also suitability of the presented basis set optimization scheme. Analogous results were obtained also for ^2P , ^2F and ^2G states. Only the ^2D states computed with [7S-6P-5D+kD] basis exhibited unsaturated behavior, as shown in Table 4. Although the states below 7^2D (regardless of their symmetry) were unaffected by the additional D functions, none of the higher ^2D states could achieve a converged excitation energy. This could mean that in such highly excited ^2D states, the Rydberg excited electron is still extensively interacting with other electrons in the ion core, yet the provided basis is no

Table 4 Comparison of correlated ground and bound state excitation energies of a neutral doublet Li above the state 7^2S for three contracted [7S-6P-5D+kL, L = D] basis sets. The ground state 2^2S energy (ROHF and CCSD) is given in a.u., while the excitation energies (EOM-CCSD) as well as the ionization potential (CCSD) are in eV

State	[7S-6P-5D]	[7S-6P-10D]	[7S-6P-14D]
2^2S ROHF	-7.4327268276	-7.4327268276	-7.4327268276
2^2S CCSD	-7.4744349730	-7.4744350378	-7.4744350426
IP CCSD	5.3877	5.3877	5.3877
7^2P	5.1070	5.1070	5.1070
7^2D	5.1097	5.1106	5.1088
8^2D		5.1745	5.1655
9^2D		5.2165	5.1750
10^2D		5.2582	5.2159
11^2D		5.2719	5.2618
12^2D		5.2828	5.2733
13^2D			5.3004
14^2D			5.3559

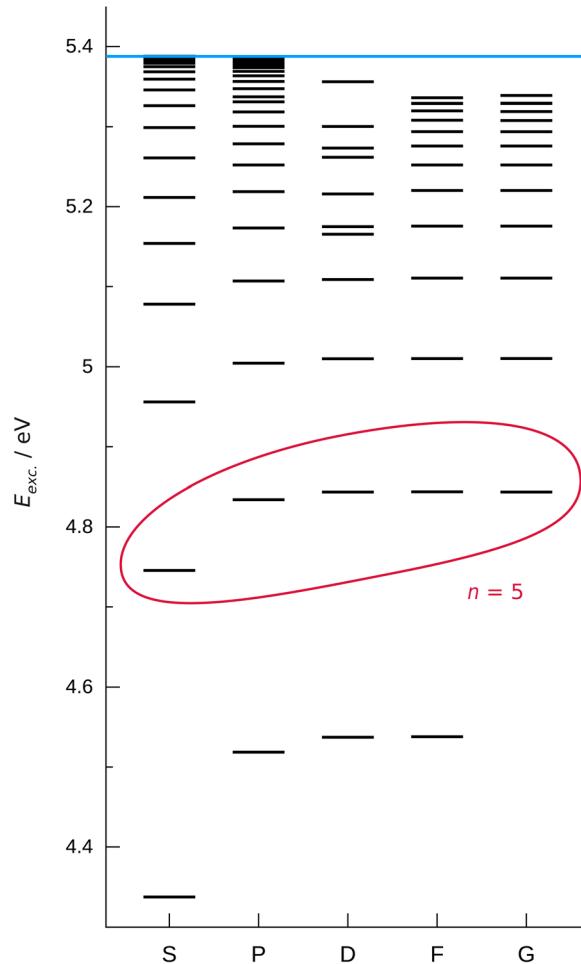


Fig. 1 Obtained EOM-CCSD excitation energy levels of ${}^2\text{Li}$ for angular momenta S up to G. Only states starting from $n = 4$ and higher are shown for better resolution of the un converged high ^2D states (see text). To help distinguish states of the same n , the states with $n = 5$ are grouped by the red oval. The level of the CCSD ionization limit is depicted in blue.

longer capable of sufficient electronic correlation description over that large distance. In contrast to the other angular



momentum states, the motion of the excited electron in ^2D states thus may not be driven by a mere positive charge of the ion core as is typical for Rydberg states. For more discussion of the high ^2D states' behaviour, see also Fig. 1 and the last paragraph of this subsection.

Moreover, for all states with the principal quantum number n larger than 7, the optimized Rydberg functions are state selective. That means, only a single specific Rydberg function needs to be added to the [7S-6P-5D] basis to achieve the appropriate correlated Rydberg state, reducing the necessary basis set size dramatically. Except for ^2D states, again, where the differences between the state selective basis and the [7S-6P-14D] basis reached even 0.1 eV, all the other L states exhibited negligible errors, from 3×10^{-9} eV for state 14 ^2G to 2×10^{-6} eV for state 10 ^2S .

Fig. 1 shows the EOM-CCSD excitation energy diagram for all the computed bound ^2S to ^2G angular momentum states starting from $n = 4$. One can clearly see the convergence of the ^2S and ^2P energy level sequences towards the CCSD ionization limit. Except for the ^2D states, which could not yet achieve converged values with respect to the basis set, as discussed in Table 4 and still commented further below, the states with higher angular momenta exhibit the same trend, yet the number of the computed energy levels is smaller. The diagram also nicely illustrates the diminishing dependence of the energy levels on the angular momentum with higher n . From $n = 5$ the ^2P , ^2D , ^2F and ^2G states are already almost aligned. Only the ^2S states keep their energy levels different even for higher n . Finally, as for the unconverged ^2D states above $n = 7$,

the figure markedly appears as if some levels were just missing while others were put in odd positions compared to the other angular momentum states of the same n . Such behaviour could suggest a poor numerical convergence of the EOM-CCSD procedure for the higher ^2D states. However, the energies converged smoothly even for a tight convergence criterion and with no significant effect on the results. Moreover, all five components of the ^2D degenerate states led to the same numerical value, despite belonging to different irreducible representations of the D_{2h} computational symmetry group. The behaviour could also be due to poorly optimized Rydberg basis functions. However, no particular issues have been experienced with optimizing the D Rydberg orbitals. Therefore, it truly seems most likely that the highly excited D electron still non-negligibly interacts with the ion core S electrons holding a weaker Rydberg character than the states in other angular momenta. In effect, such states would require an even larger set of diffuse basis functions for the saturated description of their electronic correlation, as was already suggested.

3.2 Li bound excited states

In this section, the bound Li Rydberg states computed by the EOM-CCSD method using the optimized basis are presented and compared with the best non-relativistic results known in the literature. The most appropriate data come from the systematic studies of Li ^2S , ^2P and ^2D states that employ the explicitly correlated Gaussians (ECG) and consider also the effect of the finite nuclear mass as well as the leading relativistic and QED corrections.^{21–23} These state-of-the-art studies

Table 5 Comparison of ^2S EOM-CCSD excitation energies of Li bound states obtained from the [25S-6P-5D] basis with the extensive non-relativistic ECG computations,²¹ the Full-Cl in an optimized STO basis²⁹ and the results of the Hylleraas-Cl computations.²⁹ Energy levels (E) are given in a.u., while the excitation energies (EE) as well as their differences (ΔEE) are in eV. ΔEE is defined as $EE^{[25S-6P-5D]} - EE^{\text{ref}}$. The reference 2^2S energy values in a.u. are put in parentheses for convenience. Values corresponding also to the exact non-relativistic estimate are marked with an asterisk and the bibliographic reference

State	[25S-6P-5D]		ECG ²¹		STO Full-Cl ²⁹		Hy-Cl ²⁹	
	E	EE	EE	ΔEE	EE	ΔEE	EE	ΔEE
2^2S	-7.4744350		(-7.4780603)* ²⁴		(-7.477192)		(-7.478058969)	
3^2S	-7.3505733	3.3704	3.3732* ²⁴	-0.0027	3.3727	-0.0022	3.3733	-0.0028
4^2S	-7.3150230	4.3378	4.3410* ²⁵	-0.0032	4.3406	-0.0027	4.3413	-0.0035
5^2S	-7.3000352	4.7456	4.7486* ²⁵	-0.0030	4.7486	-0.0030	4.7496	-0.0040
6^2S	-7.2923000	4.9561	4.9579* ²⁵	-0.0018	4.9595	-0.0033	4.9612	-0.0050
7^2S	-7.2878069	5.0784	5.0795* ²⁵	-0.0011	5.1047	-0.0263	5.0878	-0.0094
8^2S	-7.2850298	5.1540	5.1563	-0.0023	5.2109	-0.0569	5.1611	-0.0071
9^2S	-7.2829112	5.2116	5.2079	0.0037				
10^2S	-7.2810981	5.2610	5.2442	0.0167				
11^2S	-7.2797011	5.2990	5.2708	0.0282				
12^2S	-7.2786917	5.3264	5.2907	0.0357				
13^2S	-7.2779819	5.3457	5.3062	0.0396				
14^2S	-7.2774894	5.3592						
15^2S	-7.2771501	5.3684						
16^2S	-7.2769175	5.3747						
17^2S	-7.2767584	5.3790						
18^2S	-7.2766498	5.3820						
19^2S	-7.2765758	5.3840						
20^2S	-7.2765254	5.3854						
21^2S	-7.2764911	5.3863						
22^2S	-7.2764676	5.3870						
23^2S	-7.2764516	5.3874						
24^2S	-7.2764405	5.3877						



provide highly accurate results for most Li excited states that had ever been computed. In this work, the comparison is made only to the non-relativistic ECG results, which practically reach the estimates of the exact non-relativistic energies.^{24–28} Another comparison is made to the Hylleraas-CI (Hy-CI) study,²⁹ which provides considerably fewer 2S , 2P and 2D states. Nevertheless, the same study also presents Full-CI energies in optimal Slater-type-orbital (STO) basis that fully cover the principal quantum

number $n = 7$, covering all the states from 2^2S to 7^2S and up to 7^2I . The results for the individual angular momenta are compared in Tables 5 (2S), 6 (2P), 7 (2D), 8 (2F) and 9 (2G). The state energies are presented in a.u., while the excitation energies with respect to the ground 2^2S state are in eV rounded to 10^{-4} eV, for convenience. When appropriate, values corresponding to the estimates of the exact non-relativistic energies are labeled with a related bibliographic reference.

Table 6 Comparison of 2P EOM-CCSD excitation energies of Li bound states with respect to the ground 2^2S state obtained from the [7S-24P-5D] basis with the extensive non-relativistic ECG computations,²² the Full-CI in an optimized STO basis²⁹ and the results of the Hylleraas-CI computations.²⁹ Energy levels (E) are given in a.u., while the excitation energies (EE) as well as their differences (ΔEE) are in eV. ΔEE is defined as $EE^{[7S-24P-5D]} - EE^{\text{ref}}$. The reference 2^2S energy values in a.u. are put in parentheses for convenience. Values corresponding also to the exact non-relativistic estimate are marked with an asterisk and the bibliographic reference

State	[7S-24P-5D]		ECG ²²		STO Full-CI ²⁹		Hy-CI ²⁹	
	E	EE	EE	ΔEE	EE	ΔEE	EE	ΔEE
2^2S	-7.4744358		(-7.4780603)*, ^{24,26}		(-7.477192)		(-7.478058969)	
2^2P	-7.4065515	1.8472	1.8478* ²⁷	-0.0005	1.8660	-0.0187	1.8479	-0.0007
3^2P	-7.3336219	3.8317	3.8343	-0.0026	3.8513	-0.0196	3.8353	-0.0036
4^2P	-7.3083789	4.5186	4.5217	-0.0031	4.5391	-0.0205	4.5238	-0.0052
5^2P	-7.2967853	4.8341	4.8374	-0.0033	4.8542	-0.0201	4.8415	-0.0074
6^2P	-7.2905206	5.0046	5.0080	-0.0034	5.0245	-0.0199	5.0094	-0.0048
7^2P	-7.2867570	5.1070	5.1104	-0.0034	5.1278	-0.0208	5.1224	-0.0154
8^2P	-7.2843201	5.1733	5.1767	-0.0034				
9^2P	-7.2826463	5.2188	5.2221	-0.0033				
10^2P	-7.2814198	5.2522	5.2545	-0.0023				
11^2P	-7.2804485	5.2787						
12^2P	-7.2796394	5.3007						
13^2P	-7.2789788	5.3186						
14^2P	-7.2785302	5.3309						
15^2P	-7.2782993	5.3371						
16^2P	-7.2779292	5.3472						
17^2P	-7.2775941	5.3563						
18^2P	-7.2773332	5.3634						
19^2P	-7.2771260	5.3691						
20^2P	-7.2769625	5.3735						
21^2P	-7.2768372	5.3769						
22^2P	-7.2767405	5.3796						
23^2P	-7.2766658	5.3816						
24^2P	-7.2766082	5.3832						
25^2P	-7.2765638	5.3844						

Table 7 Comparison of 2D EOM-CCSD excitation energies of Li bound states with respect to the ground 2^2S state obtained from the [7S-6P-14D] basis with the extensive non-relativistic ECG computations,²³ the Full-CI in an optimized STO basis²⁹ and the results of the Hylleraas-CI computations.²⁹ Energy levels (E) are given in a.u., while the excitation energies (EE) as well as their differences (ΔEE) are in eV. ΔEE is defined as $EE^{[7S-6P-14D]} - EE^{\text{ref}}$. The reference 2^2S energy values in a.u. are put in parentheses for convenience. Values corresponding also to the exact non-relativistic estimate are marked with an asterisk and the bibliographic reference

State	[7S-6P-14D]		ECG ²³		STO Full-CI ²⁹		Hy-CI ²⁹	
	E	EE	EE	ΔEE	EE	ΔEE	EE	ΔEE
2^2S	-7.4744350		(-7.4780603)*, ^{24,26}		(-7.477192)		(-7.478058969)	
3^2D	-7.3320162	3.8754	3.8786* ²⁷	-0.0032	3.8937	-0.0183	3.8789	-0.0035
4^2D	-7.3076902	4.5373	4.5408	-0.0034	4.5560	-0.0187	4.5402	-0.0028
5^2D	-7.2964306	4.8437	4.8472	-0.0035	4.8624	-0.0187	4.8482	-0.0045
6^2D	-7.2903160	5.0101	5.0137	-0.0036	5.0288	-0.0187	5.0167	-0.0066
7^2D	-7.2866912	5.1088	5.1140	-0.0053	5.1291	-0.0204	5.1226	-0.0138
8^2D	-7.2846058	5.1655						
9^2D	-7.2842566	5.1750						
10^2D	-7.2827529	5.2159						
11^2D	-7.2810660	5.2618						
12^2D	-7.2806438	5.2733						
13^2D	-7.2796484	5.3004						
14^2D	-7.2776090	5.3559						



Table 8 Comparison of ^2F EOM-CCSD excitation energies of Li bound states with respect to the ground $2\ ^2\text{S}$ state obtained from the [7S-6P-5D-13F] basis with estimates of the exact non-relativistic values²⁸ and the Full-CI results in an optimized STO basis.²⁹ Energy levels (E) are given in a.u., while the excitation energies (EE) as well as their differences (ΔEE) are in eV. ΔEE is defined as $EE^{[7S-6P-5D-13F]} - EE^{\text{ref}}$. The reference $2\ ^2\text{S}$ energy values in a.u. are put in parentheses for convenience. Values corresponding to the exact non-relativistic estimate are marked with an asterisk and the bibliographic reference

State	[7S-6P-5D-13F]		Exact non-rel. est. ²⁸		STO Full-CI ²⁹	
	E	EE	EE	ΔEE	EE	ΔEE
$2\ ^2\text{S}$	-7.4744350		(-7.4780603)* ²⁴		(-7.477192)	
$4\ ^2\text{F}$	-7.3076701	4.5379	4.5414* ²⁸	-0.0035	4.5329	0.0050
$5\ ^2\text{F}$	-7.2964194	4.8440	4.8475* ²⁸	-0.0035	4.8396	0.0045
$6\ ^2\text{F}$	-7.2903080	5.0103			5.0064	0.0040
$7\ ^2\text{F}$	-7.2866230	5.1106			5.1100	0.0006
$8\ ^2\text{F}$	-7.2842313	5.1757				
$9\ ^2\text{F}$	-7.2825915	5.2203				
$10\ ^2\text{F}$	-7.2814185	5.2522				
$11\ ^2\text{F}$	-7.2805499	5.2759				
$12\ ^2\text{F}$	-7.2798861	5.2939				
$13\ ^2\text{F}$	-7.2793602	5.3082				
$14\ ^2\text{F}$	-7.2789311	5.3199				
$15\ ^2\text{F}$	-7.2785961	5.3290				
$16\ ^2\text{F}$	-7.2783444	5.3359				

Table 5 shows the ^2S states computed with the [25S-6P-5D] basis. We can see that the ground state energy of the present study is still more than 3 millihartree above the highly precise computations. This is well understandable due to the Gaussian character of the basis, lack of any explicit electronic correlation, only the CCSD level of theory describing the three-electron system and also the relatively small basis size. Nevertheless, when we compare the excitation energies, we can see that the present Gaussian basis results are consistently only a few meV off the ECG values up to the state $8\ ^2\text{S}$. From the state $9\ ^2\text{S}$, the differences increase (even change the sign) and one might speculate that the error could reach up to tens of meV for the highest computed state $24\ ^2\text{S}$. Such a sudden drop in accuracy may be put down to the higher D orbital space insufficiency, as discussed with the Table 4 and Fig. 1, since the D functions contribute to the ^2S states correlation energy *via* double excitations. On the other hand, there is an apparent convergence of the excitation energies to the CCSD ionization limit, which is just 4 meV below the experimental value. By taking this into account, the error estimate for the highest achieved excitation energies with respect to the accurate non-relativistic values may still fall in the interval of only a few meV. The results are also consistent within a few meV with the Hy-CI and with the STO Full-CI excitation energies except that the latter deviates from the precise ECG values for its highest $7\ ^2\text{S}$ and $8\ ^2\text{S}$ states by an order of magnitude more than the Gaussian basis results of the present study.

In Table 6, we can see that the ^2P results in the basis [7S-24P-5D] are remarkably close to the ECG values within meV accuracy, while the STO Full-CI excitation energies differ from the present calculations by an order of magnitude more. It can also be noticed that the present Gaussian excitation energies are all closer to the ECG results and with a very consistent difference compared to the Hy-CI values. From this trend and from the apparent convergence towards the IP limit like in the ^2S states, we might speculate that the accuracy of the computed excitation energy of the highest achieved $25\ ^2\text{P}$ state could also be within a few meV.

Similarly in Table 7, the ^2D states obtained from the [7S-6P-14D] basis are closest to the ECG results with consistent differences in meV, while the differences from the Hy-CI values are slightly less regular. The STO Full-CI excitation energies, again, differ from the present results by an order of magnitude more than the ECG values. The excitation to the state $7\ ^2\text{D}$ (the highest ^2D state achieved by all three comparative studies) exhibits sudden deviation from the three reference results. This, again, reflects the insufficiency of the developed basis for a proper correlated description of the higher ^2D states as discussed in Table 4 and Fig. 1.

As for the ^2F states (Table 8), computed in the [7S-6P-5D-13F] basis, there are not many studies to compare with. The estimates of the exact non-relativistic values are taken from a relatively old review article by King.²⁸ The differences between the estimates and the present results are within a few meV, which is still on a par with the precise ECG studies of

Table 9 Comparison of ^2G EOM-CCSD excitation energies of Li bound states with respect to the ground $2\ ^2\text{S}$ state obtained from the [7S-6P-5D-12G] basis with the Full-CI results in an optimized STO basis.²⁹ Energy levels (E) are given in a.u., while the excitation energies (EE) as well as their differences (ΔEE) are in eV. ΔEE is defined as $EE^{[7S-6P-5D-12G]} - EE^{\text{ref}}$. The reference $2\ ^2\text{S}$ energy value in a.u. is put in parentheses for convenience

State	[7S-6P-5D-12G]		STO Full-CI ²⁹	
	E	EE	EE	ΔEE
$2\ ^2\text{S}$	-7.4744350		(-7.477192)	
$5\ ^2\text{G}$	-7.2964303	4.8437	4.8371	0.0066
$6\ ^2\text{G}$	-7.2903074	5.0104	5.0041	0.0062
$7\ ^2\text{G}$	-7.2866226	5.1106	5.1045	0.0061
$8\ ^2\text{G}$	-7.2842310	5.1757		
$9\ ^2\text{G}$	-7.2825914	5.2203		
$10\ ^2\text{G}$	-7.2814184	5.2522		
$11\ ^2\text{G}$	-7.2805500	5.2759		
$12\ ^2\text{G}$	-7.2798892	5.2938		
$13\ ^2\text{G}$	-7.2793766	5.3078		
$14\ ^2\text{G}$	-7.2789649	5.3190		
$15\ ^2\text{G}$	-7.2785953	5.3291		
$16\ ^2\text{G}$	-7.2782391	5.3388		



Adamowicz *et al.*^{21–23} for the 2S , 2P and 2D states. The STO Full-CI results also differ by only a few meV, although with the opposite sign. The reason why the 2F excitation energies are this close to the STO Full-CI results in contrast to the 2S , 2P or 2D states may be due to a true Rydberg character of the 2F states.

The only reference data for the 2G states in Table 9 that we can compare to are those from the STO Full-CI computations. Similarly like for the 2F states, the results differ in the order of meV, although there are only three excited states available for comparison.

4 Conclusions

For an *ab initio* quantum chemical description of Li Rydberg states, an appropriate diffuse Gaussian basis was developed by a variational optimization of virtual orbitals of the corresponding Li^+ ion core. The approach is based on Koopmans' theorem, which says that a virtual orbital of a closed shell system describes a captured electron, which actually means a Rydberg state. The resulting basis consists of the standard aug-ano-pVQZ set for sufficient description of the electronic correlation, an extra high-exponent contracted function to achieve a high-quality Hartree-Fock field and a set of optimal diffuse Rydberg functions.

At the EOM-CCSD level of theory, a minimal subset of the optimized basis could be found, for which the ionization potential and the excitation energies were converged with respect to the number of the Rydberg functions used. Higher Rydberg states could be effectively achieved by a state-selective inclusion of the corresponding Rydberg function, dramatically reducing the demands on the basis set size.

Dozens of states at high accuracy could be achieved by the present approach, namely, up to the states $24\ ^2S$, $25\ ^2P$, $14\ ^2D$, $16\ ^2F$ and $16\ ^2G$, that is many more than by competitive *ab initio* methods. Compared to the state-of-the-art ECG approach, the computed excitation energies consistently differed mostly in the order of meV. Only the 2D states above $6\ ^2D$ could not achieve convergence, which might be due to their supposedly weak Rydberg character. The results were also comparable to Hylleraas-CI energies; however, the differences were less regular than with the ECG values. Nevertheless, the presented excitation energies even surpassed accuracy of Full-CI results computed in an optimal STO basis by an order of magnitude.

Regardless of the excellent quality of the presented basis, plenty of room for improvement remains. The number of primitive functions is still too large for practical use in standard quantum chemistry codes, which typically impose various restrictions on the basis set size. The optimization process could also be more sophisticated, involve directly more virtual orbitals and the basis could use more flexible parameterization than ETG, *e.g.*, ExTG.³ On the other hand, not all chemical systems would require this high accuracy for the excited states, so the optimization criteria might appropriately loosen.

Although the study was performed on the lithium atom, the approach is universal for any ion core + electron system

including such with an open-shell ion core, as long as the appropriate canonical RHF or ROHF^{5–8} orbitals are used. This method could also be applied to molecules, where, however, still more research needs to be done on several fronts to assess its suitability or the need for more development. For example, the question of multiple Rydberg centers in a single molecule, the question of strong coupling of low-lying states with the ion core or the question of states with otherwise complicated character. Also, performing Rydberg basis optimization specifically for a given molecule should lead to smaller yet superior molecular basis sets than using the basis optimized just for an isolated atom. All these questions, however, would require more dedicated studies. Similarly, the method is not limited to Gaussian basis sets but can be applied to any basis set types. Once the presented tailored basis set generation process becomes sufficiently tuned so that it is feasible for common quantum chemistry codes, it could promise an affordable highly accurate approach to *ab initio* state-selective investigation of molecular Rydberg states and possibly also of their related resonances.

Conflicts of interest

There are no conflicts of interest to declare.

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