Studies on the hollow states of atomic lithium by a density functional approach

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Abstract

Density functional calculations are performed for twelve $2l'l''n''$ ($n\geq2$) triply excited hollow resonance series of Li, viz., $2s^2ns^2S^e$, $2s^2np^2P_o$, $2s^2nd^2D_e$, $2p^2ns^2D^e, 2s2pns^4P_o$, $2s2pn^2P_e$, $2p^2np^2F_o, 4P_o$, $2p^2nd^2G_e, 4P_e$ and $2s2pnd^4P_o$, covering a total of about 270 low-, moderately high- and high-lying states, with $n$ as high as up to 25. The work-function-based exchange potential and the nonlinear gradient plus Laplacian included Lee-Yang-Parr correlation energy functional is used. The relevant Kohn-Sham-type equation is solved numerically using the generalized pseudospectral method offering nonuniform, optimal spatial discretization to obtain the orbitals and densities. The present single determinantal approach yields fairly accurate results for the nonrelativistic energies, excitation energies as well as the radial densities and other expectation values. Except for the one state, the discrepancy in the calculated state energies remains well within 0.98%, whereas the excitation energies deviate by 0.02–0.58% compared to the available experimental and other theoretical results. Additionally companion calculations are also presented for the 37 $3l'l''n''$ ($n\geq3$) doubly hollow states (seven are $n=3$ intrashell type) of Li with both K and L shells empty (up to $n=6$) in the photon energy range 175.63–180.51 eV, with varying symmetries and multiplicities. Our calculation shows good agreement with the recent literature data for the only two such doubly hollow states reported so far, viz., $3s^23p^2P^o$ and $3s3p^2 4P^e$. The resonance series are found to be inextricably entangled to each other, leading to complicated behavior in their positions. Many new states are reported here for the first time. This provides a simple, efficient and general scheme for the accurate calculation of these and other multiply excited Rydberg series of many-electron atomic systems within density functional theory.

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I. INTRODUCTION

Triply excited states of atomic lithium represent the prototypical case of a highly correlated, multi-excited three-electron system in the presence of a nucleus, and thus typify the four-body Coulombic problem. Since all the three electrons reside in higher shells leaving the K shell empty, these are often referred to as the hollow states. As the one-step photogeneration of such a state requires coherent excitation of all the three electrons, these are usually more difficult to produce from the ground state by single photon absorption or electron impact excitation. These, in addition to their proximity to more than one thresholds coupled with the presence of an infinite number of open channels associated with these resonances, have offered considerable challenges to both experimentalists as well as theoreticians.

The recent advances in third-generation, extreme-UV synchrotron radiation sources as well as the availability of sophisticated and powerful quantum mechanical methodologies have stimulated an overwhelming amount of works in the last decade that shed significant light on the understanding of such systems with greater accuracy. Ever since the first observation of $2l'2l''l''$ states of Li in a beam-foil experiment [1], numerous attempts [2-4] have been made over the years to use this technique which identified bound states such as the $2p^3 4S^o$ besides many autoionizing states. Later, photoabsorption spectroscopy [5] using a dual laser plasma technique reported measurement of the lowest $2s^22p 2P^o$ resonance in Li. Subsequently a large number of higher resonances were found and tentatively classified in a wider energy range (140–165 eV) [6-8]. First high-precision photoelectron spectroscopic determination [9] of the partial photoionization cross sections generated tremendous interest to measure the resonance positions, widths of both even- and odd-parity hollow states having varied symmetries [10-14] with better resolution over wider energy regions. Some Rydberg series [15] as well as the states with both K and L shell vacancies [8,13] have also been identified lately.

Parallel to the experimental progresses, a substantial amount of theoretical works have also been done over the years for reliable, accurate prediction of energies, widths and lifetimes of these multi-excited states, varying in their complexity and accuracy. One of the earliest such calculations for Li-isoelectronic series was due to [16] employing a truncated diagonalization method (TDM), based on the hydrogenic orbitals. Later other formalisms such as the $1/Z$ expansion method [17], many-body perturbation theory [18] were also used.
to investigate these states. Some other recent theoretical works include the state-specific theory [19-21], the configuration interaction (CI) type approach [22], joint saddle point (SP) and complex coordinate rotation (CCR) method [23-25], the space partition and stabilization procedure [26], a density functional formalism [27], several variants of the R-matrix theory [28-31] as well as the TDM [32,33], the hyperspherical coordinate approach [34,35], etc. Although the most natural and commonest choice in these works was neutral atom (Li), other atomic systems such as the negative ions (e.g., He$^-$), positive ions like Li-isoelectronic series or N$_2^+$ [22] have also received considerable attention. While majority of the available formalisms involve traditional wave-function-based calculations requiring large basis sets and often involving mixing of continuum states, a density-based formalism for triply excited states was proposed in [27]. In this approach a Kohn-Sham (KS) type differential equation was solved to obtain the self-consistent set of orbitals and densities using the nonvariational local work-function based exchange potential [36] in conjunction with the nonlinear gradient- and Laplacian-included correlation energy functional of Lee, Yang and Parr (LYP) [37]. Fairly good quality results were reported for various closed and open shell many-electron atomic excited states including the single, double, triple as well as low and moderately high excitations; core and valence states; bound and autoionizing states besides the satellite states [38-43,27]. This single-determinantal formalism was able to reproduce the excited state energies, radial densities, various expectation values, excitation energies (10–2000 eV) as well as the small energy differences (0.03–23.5 eV) quite satisfactorily. However, all the above density functional theory (DFT)-based calculations of atomic excited states employed a Numerov-type finite difference (FD) scheme to numerically solve the KS type equation. Recently a generalized pseudospectral (GPS) approach has been utilized to solve it in a more accurate and efficient manner [44], as demonstrated for the singly and doubly excited high-lying Rydberg states of He as well as the singly excited states of Li and Be. The singly excited state energies were within 0.01% of the best literature data for He (for other atoms it was less than 0.02%), while for the doubly excited states of He it was well within 3.6%. The discrepancy in the calculated single and double excitation energies for 31 selected states were within 0.009–0.632% and 0.085–1.600% respectively.

The GPS method has been shown to be a very powerful tool for accurate and physically meaningful results of both static and dynamic properties of Coulombic singular systems such as atoms and molecules as well as other stronger singularities like the generalized
while in [27], results were presented for all the eight n=2 intrashell triply excited states of Li isoelectronic series (Z=2,3,4,6,8,10) with reasonable accuracy, resonance series including the higher members were not considered and to the best of our knowledge, no other DFT-based attempts are known so far for these systems. The purpose of this work is therefore to explore and extend the regions of validity of the density-based approach to these challenging hollow states and also to study the spectra of these resonances in a detailed and elaborate way. We thus focus on the energies and the excitation energies of twelve 2l2l'nll'' (n≥2) odd- and even-parity doublet and quartet resonance series of Li leading nearly to 270 states (2s2ns 2S0, 2s2np 2P0, 2s2nd 2D0, 2p2ns 2D0, 4P0, 2s2pns 4P0, 2s2pnp 4D0, 2p2np 2F0, 4F0, 2p2nd 2G0, 4F0, 2s2pnd 4F0), up to a maximum of n=25. As a further test, additional results are also reported for 37 3l3l'nll'' (n≥3) doubly hollow states of Li having vacancies in both the K and L shells up to n=6, out of which seven are n=3 intrashell type. Comparisons are made with the experimental and other theoretical results, wherever possible. The article is organized as follows: Section II presents a brief summary of the methodology as well as the computational aspects. Section III makes a detailed discussion on the obtained results and a few conclusions are drawn in section IV.

II. METHODOLOGY

Since the work-function formalism for atomic excited states [38-43,27] as well as its GPS implementation [44] has been discussed in detail previously, here we give only the essential steps in the calculation (atomic units employed throughout the article, unless otherwise mentioned).

The local exchange potential with which the electrons move is interpreted [36,49] physically as the work done to move an electron from infinity to its position r against the electric field \( E_x(r) \) arising out of the Fermi-hole charge distribution, \( \rho_x(r,r') \), and as such is given by the following line integral,

\[
v_x(r) = - \int_{\infty}^{r} E_x(r) \cdot dl.
\] (1)

This field \( E_x(r) \), being representative of the Pauli correlation, as its quantum mechanical source charge distribution is the pair correlation density, has the following form,

\[
E_x(r) = \int \frac{\rho_x(r,r')(r-r')}{|r-r'|^3} dr.
\] (2)
This work against $E_x(r)$ can be determined exactly as the Fermi hole is known explicitly in terms of the single-particle orbitals,

$$\rho_x(r, r') = -\frac{|\gamma(r, r')|^2}{2\rho(r)},$$

where

$$\gamma(r, r') = \sum_i \phi_i^*(r)\phi_i(r').$$

denotes the single-particle density matrix spherically averaged over coordinates of the electrons of a given orbital angular momentum quantum number. Now within the central-field approximation, the orbitals expressed as $\phi_i(r) = R_{nl}(r) Y_{lm}(\Omega)$ ($Y_{lm}(\Omega)$ denoting the usual spherical harmonics), give the total electron density as the sum of the occupied orbitals,

$$\rho(r) = \sum_i |\phi_i(r)|^2.$$ 

and the spherically averaged radial component of the electric field is simplified as,

$$E_{x,r}(r) = -\frac{1}{4\pi} \int \rho_x(r, r') \frac{\partial}{\partial r} \frac{1}{|r - r'|} \, dr'd\Omega.'$$

Now assuming that a unique local exchange potential exists for a given excited state, the following KS-type equation is solved,

$$\left[-\frac{1}{2} \nabla^2 + v_{es}(r) + v_{xc}(r)\right] \phi_i(r) = \varepsilon_i \phi_i(r),$$

to obtain the self-consistent set of orbitals $\{\phi_i\}$ and the electron density. Here $v_{es}(r)$ denotes the usual Hartree electrostatic potential consisting of the electron-nuclear attraction and the interelectronic Coulomb repulsion,

$$v_{es}(r) = -\frac{Z}{r} + \int \frac{\rho(r')}{|r - r'|} \, dr'$$

and $v_{xc}(r)$, the total exchange-correlation (XC) potential is partitioned as,

$$v_{xc}(r) = v_x(r) + v_c(r)$$

While $v_x(r)$ can be accurately determined as outlined above, the accurate form of $v_c(r)$ valid for a general excited state is unknown as yet and therefore requires to be approximated.

There are several prescriptions available in the literature and the present work uses the widely used LYP functional [37].
Now we present a brief overview of the computational procedure used to solve the pertinent KS equation through the GPS formalism. One disquieting feature of the commonly used equal-spacing FD methods is that because of the existence of Coulomb singularity at the origin as well as the long range nature of the Coulomb potential, one requires a large number of grid points to achieve reasonably good accuracy even for the ground states. However the GPS method allows nonuniform and optimal spatial discretization maintaining similar accuracy at both small and large $r$ regions. Thus one can work with a much lesser grid points having a denser mesh at small $r$ while a coarser mesh at large $r$. Moreover it also has the attractive feature of possessing both the simplicity of direct FD or finite element methods and the fast convergence of the finite basis set methods.

One of the principal features of this scheme lies in the fact that a function $f(x)$ defined in the interval $x \in [-1, 1]$ can be approximated by the polynomial $f_N(x)$ of order $N$ so that,

$$f(x) \cong f_N(x) = \sum_{j=0}^{N} f(x_j) \, g_j(x),$$

and the approximation is exact at the collocation points $x_j$, i.e.,

$$f_N(x_j) = f(x_j).$$

Here we employ the Legendre pseudospectral method using $x_0 = -1, \, x_N = 1$, where $x_j (j = 1, \ldots, N-1)$ are obtainable from the roots of the first derivative of the Legendre polynomial $P_N(x)$ with respect to $x$, i.e.,

$$P'_N(x_j) = 0.$$

The cardinal functions, $g_j(x)$ in Eq. (9) are given by the following expression,

$$g_j(x) = -\frac{1}{N(N + 1)P_N(x_j)} \frac{(1 - x^2) P'_N(x)}{x - x_j},$$

obeying the unique property $g_j(x_j') = \delta_{j,j'}$. Now the semi-infinite domain $r \in [0, \infty]$ is mapped into the finite domain $x \in [-1, 1]$ by the transformation $r = r(x)$. One can make use of the following algebraic nonlinear mapping [50,51],

$$r = r(x) = L \frac{1 + x}{1 - x + \alpha},$$

where $L$ and $\alpha = 2L/r_{\text{max}}$ may be termed as the mapping parameters. Now, introducing the following relation,

$$\psi(r(x)) = \sqrt{r'(x)} f(x)$$
coupled with the symmetrization procedure [50,51] leads to the following coupled set of equations,

\[
\sum_{j=0}^{N} \left[ -\frac{1}{2} D^{(2)}_{jj} + \delta_{jj} v(r(x_j)) + \delta_{jj} v_m(r(x_j)) \right] A_j = E A_j', \quad j = 1, \ldots, N - 1,
\]

(15)

where

\[
A_j = \left[ r'(x_j) \right]^{1/2} \psi(r(x_j)) \left[ P_N(x_j) \right]^{-1}.
\]

(16)

and the symmetrized second derivative of the cardinal function, \( D^{(2)}_{jj} \) is given by,

\[
D^{(2)}_{jj} = \left[ r'(x_{jj}) \right]^{-1} d^{(2)}_{jj} \left[ r'(x_j) \right]^{-1},
\]

(17)

with

\[
d^{(2)}_{j',j} = \frac{1}{r'(x_j)} \frac{(N+1)(N+2)}{6(1-x_j)^2} \frac{1}{r'(x_j)} \quad j = j',
\]

\[
= \frac{1}{r'(x_{jj})} \frac{1}{(x_j - x_{jj})^2} \frac{1}{r'(x_{jj})} \quad j \neq j'.
\]

(18)

Note the advantage that this leads to a symmetric matrix eigenvalue problem which can be readily solved to give accurate eigenvalues and eigenfunctions.

Within the central-field approximation, taking the exchange potential in Eq. (1) and the LYP correlation functional [37], KS equation (6) is solved numerically in a self-consistent manner to obtain the orbitals. These are then employed to construct the various Slater determinants derived from a particular electronic configuration. In general, denoting the electronic energies of determinants and multiplets associated with a given electronic configuration by \( E(D_i) \) and \( E(M_i) \) respectively, the Slater’s diagonal sum rule [52,38-44,27] is used to calculate the \( E(M_i) \) as,

\[
E(M_j) = \sum_i A_{ji} E(D_i).
\]

(19)

For all the calculations reported in this work, a consistent convergence criteria of \( 10^{-6} \) and \( 10^{-8} \) a.u., are used for the potential and energy respectively, whereas a maximum of 500 radial grid points sufficed to achieve convergence.
III. RESULTS AND DISCUSSION

The calculated nonrelativistic term and excitation energies for various hollow states of Li along with the available experimental and theoretical results are given in tables I through VII. In the literature, usually the excitation energies are reported, while the individual state energies are given in only few occasions. In a recent study of the low-lying singly excited states of several open-shell atoms (B, C, O, F, Na, Mg, Al, Si, P and Cl) within the work-function formalism [42], it was observed that the excitation energies from the exchange-only and the numerical Hartree-Fock (HF) calculations showed good agreement with each other. Interestingly however, the two correlation energy functionals (relatively simpler local Wigner and the nonlocal LYP) did not show any considerable improvements in excitation energies, although the excited-state energies were improved significantly. Therefore we decided to present both these quantities for all the states considered in this work. The state energies are given in atomic units, while the excitation energies in eV (1 a.u. = 27.2076544 eV) are given relative to the accurate ground state of Li calculated from a full core plus correlation using the multiconfiguration interaction wave function, i.e., $-7.47805953$ a.u. [54], for a consistent comparison with the literature data. Here we note that the present calculated ground state energy of Li is $-7.4782839$ a.u. The independent particle model classification [32,33] is used throughout the article, where the six core Li$^+$ $n=2$ intrashell doubly excited states, viz., $2s^2 \, 1S_e$, $2s2p \, 3P_o$, $2p^2 \, 3P_e$, $2p^2 \, 1D_e$, $2s2p \, 1P_o$ and $2p^2 \, 1S_e$ are denoted by A, B, C, D, E and F respectively. Only the state energies were reported in [33], so their excitation energies quoted in this work for comparison were calculated from the same Li ground state as mentioned above. The excitation energies in [31] were given with respect to the first excited $1s^2 \, 2P_o$ state of Li and thus to put things in proper perspective, we have used $E[1s^22p \, 2P_o-1s^22s \, 2S_e]$=1.848 eV to obtain the respective resonance positions relative to the Li ground state.

Now table I tabulates the results for even-parity $(A,ns) \, 2S_e$ and odd-parity $(A,np) \, 2P_o$, n=2–22 hollow states of Li. The experimental results for $2S_e$ resonances are yet to be obtained. The lower members of the series have been treated theoretically in considerable detail by several workers employing a multitude of techniques, e.g., the n=3 state by a hyperspherical coordinate method [35], the n=3,4 resonances by a combination of SP and CCR method [25]. The n=3–9 resonances were also calculated by the R-matrix method.
including a set of core base states for the Li$^+$ target along with an optimization of the collisional representation [28]. Recently, an eigenphase derivative technique in conjunction with a quantum defect theory [31] reported the low and high resonances up to n=22, whereas the same up to n=12 have been studied through the TDM [33]. The agreement of the present density functional results for both the quantities are seen to be fairly good; the current state energies lie about 0.36–0.88% above the TDM results [33], whereas the excitation energies are higher by 0.41–0.51% from those of [31]. It is noted that the small differences in excitation energies are reproduced quite nicely within the whole series; a feature which holds true for all the resonance series dealt in this work. Coming to the $^2\text{P}^o$ states, these are the most widely studied hollow resonance series in Li, both experimentally and theoretically, chiefly due to the fact that the lowest n=2 intrashell Li state is the $2s^22p\ ^2\text{P}^o$. Photoion yield spectroscopic measurements determined its position at 142.33 eV [7] and 142.35 eV [6] respectively, which has been supported by various theoretical calculations, e.g., the combined SP CCR method [23], the complex scaling method having correlated basis functions constructed from B-splines [53], the R-matrix method [28], as well as the TDM method [33]. Our calculation gives an excitation energy of 142.385 eV which is only 0.02% above the experimental results. It may be noted that the HF energy of the lowest resonance is $-2.16954$ a.u. [18], which matches almost exactly with the present exchange-only result of $-2.1694$ a.u., (0.00014 a.u., deviation) illustrating the fact that the exchange contribution is included quite accurately within this formalism. Other members of the series with n=3–7 show good agreement with the CCR calculation [24]. For n=8–11, the term energies are available also through the TDM calculation [33] and fairly good agreement is noticed in our results with those. The present term energies are underestimated by 0.24–0.98% with respect to the CCR results [23,24], leading to higher excitation energies (the deviations with respect to [28], [29] being 0.05–0.32% and 0.43–0.46% for n=2–9 and n=3–10 respectively). No results could be found for the resonances with n≥12.

Now in Table II, we compare the even-parity $\langle A,nd \rangle$ and $\langle D,ns \rangle \ ^2\text{D}^e$ hollow states of Li arising from electronic configurations $2s^2nd$ and $2p^2ns$ having n=24 and 25 respectively with the existing literature data. No experimental results have been reported so far for the former series to the best of our knowledge, whereas only the lowest state of the latter series has been observed. It lies at 144.77 eV in the photoelectron spectroscopy [11] and our result matches excellently with this (the excitation energy is only 0.043 eV lower than the experimental
TABLE I: Comparison of the state (in a.u.) and excitation energies (in eV) relative to the Li ground state [54], of 2s\(^2\)2n\(^1\)S\(_e\) and 2s\(^2\)2n\(^1\)P\(_o\) resonances of Li. PW signifies present work.

| n  | \(\langle A,ns \rangle{^2S_e}\) | Excitation energy(eV) | \(\langle A,np \rangle{^2P_o}\) | Excitation energy(eV) |
|----|-------------------------------|----------------------|-------------------------------|----------------------|
|    | PW Ref. | \(-E\)(a.u.) | PW Ref. | \(-E\)(a.u.) | PW Ref. | \(-E\)(a.u.) | PW Ref. |
| 2  |         | 2.2448 |                         | 2.2503\(^c\), 2.247\(^b\), 2.2428\(^c\) | 142.385 | 142.255\(^e\), 142.439\(^e\), 142.12\(^d\), 142.310\(^e\), 142.35\(^d\), 142.33\(^g\) |
| 3  | 1.9871 | 2.0048 | 149.396 | 148.632\(^e\), 148.822\(^c\), 1.9740 | 1.9935\(^b\), 1.991\(^b\), 1.9879\(^c\) | 149.253 | 149.211\(^d\), 149.07\(^b\), 149.222\(^c\), 149.374\(^c\) |
| 4  | 1.9402 | 1.9509 | 150.762 | 150.381\(^c\), 150.181\(^e\), 1.9321 | 1.9480\(^b\), 1.9423\(^c\) | 150.893 | 150.480\(^i\), 150.24\(^k\), 150.615\(^c\), 150.397\(^c\) |
| 5  | 1.9194 | 1.9265 | 151.238 | 150.600\(^i\), 150.045\(^c\), 1.9160 | 1.9319\(^b\), 1.9241\(^c\) | 151.331 | 150.917\(^b\), 150.67\(^b\), 151.110\(^b\), 150.836\(^c\) |
| 6  | 1.9094 | 1.9165 | 151.510 | 150.855\(^i\), 151.317\(^c\), 1.9075 | 1.9214\(^b\), 1.9145\(^c\) | 151.562 | 151.203\(^d\), 150.88\(^k\), 151.371\(^c\), 151.057\(^c\) |
| 7  | 1.9037 | 1.9111 | 151.665 | 151.092\(^i\), 151.570\(^c\), 1.9027 | 1.9160\(^b\), 1.9098\(^c\) | 151.692 | 151.349\(^i\), 151.03\(^k\), 151.499\(^c\), 151.210\(^c\) |
| 8  | 1.9004 | 1.9072 | 151.755 | 151.173\(^c\), 151.263\(^c\), 1.8996 | 1.9068\(^c\) | 151.777 | 151.11\(^b\), 151.581\(^c\), 151.285\(^c\) |
| 9  | 1.8980 | 1.9052 | 151.820 | 151.151\(^i\), 151.624\(^c\), 1.8976 | 1.9048\(^c\) | 151.831 | 151.16\(^b\), 151.635\(^c\), 151.337\(^c\) |
| 10 | 1.8965 | 1.9037 | 151.861 | 151.190\(^i\), 151.665\(^c\), 1.8961 | 1.9034\(^c\) | 151.872 | 151.20\(^b\), 151.673\(^c\) |
| 11 | 1.8953 | 1.9026 | 151.894 | 151.226\(^i\), 151.695\(^c\), 1.8950 | 1.9024\(^c\) | 151.902 | 151.701\(^c\) |
| 12 | 1.8944 | 1.9018 | 151.918 | 151.247\(^i\), 151.717\(^c\), 1.8943 |                         | 151.921 |                         |
| 13 | 1.8935 | 1.9001 | 151.953 | 151.264\(^c\), 1.8937 |                         | 151.937 |                         |
| 14 | 1.8935 | 1.9001 | 151.953 | 151.264\(^c\), 1.8937 |                         | 151.937 |                         |
| 15 | 1.8929 | 1.9001 | 151.953 | 151.288\(^c\), 1.8937 |                         | 151.937 |                         |
| 16 | 1.8925 | 1.9001 | 151.953 | 151.288\(^c\), 1.8937 |                         | 151.937 |                         |
| 17 | 1.8923 | 1.9001 | 151.953 | 151.288\(^c\), 1.8937 |                         | 151.937 |                         |
| 18 | 1.8921 | 1.9001 | 151.953 | 151.288\(^c\), 1.8937 |                         | 151.937 |                         |
| 19 | 1.8919 | 1.9001 | 151.953 | 151.288\(^c\), 1.8937 |                         | 151.937 |                         |
| 20 | 1.8917 | 1.9001 | 151.953 | 151.288\(^c\), 1.8937 |                         | 151.937 |                         |
| 21 | 1.8915 | 1.9001 | 151.953 | 151.288\(^c\), 1.8937 |                         | 151.937 |                         |
| 22 | 1.8914 | 1.9001 | 151.953 | 151.288\(^c\), 1.8937 |                         | 151.937 |                         |

\(^a\)Reference [23].
\(^b\)Reference [24].
\(^c\)Reference [33].
\(^d\)Reference [10].
\(^e\)Reference [28].
\(^f\)Reference [6].
\(^g\)Reference [7].
\(^h\)Reference [35].
\(^i\)Reference [31].
\(^j\)Reference [24].
\(^k\)Reference [29].
\(^l\)Reference [25].
values with a deviation of 0.03%). Both the hyperspherical coordinate approach [35] as well as the TDM [33] give the energy of 2s\(^2\)3d state at \(-1.9614\) a.u., whereas the CCR value is \(-1.9659\) a.u. [25]. These are to be compared with the present value of \(-1.9461\) a.u. The CCR results are also available for the \(\langle D,ns \rangle\) series having \(n=2,3\). It is noticed that for the former series, the state energies are underestimated in all cases with respect to the TDM results, whereas for the latter, the same is overestimated for \(n=2,4-7\) (\(n=8\) shows complete agreement). This overestimation could occur either because of (a) the nonvariational nature of the exchange potential employed and/or (b) the inadequacy of the LYP correlation energy functional used. Resonances up to 9 for both the series were earlier reported in the R-matrix calculation [28]. The absolute per cent deviation of the \(\langle A,nd \rangle\) (\(n=3-11\)) and \(\langle D,ns \rangle\) (\(n=2-9\)) state energies are 0.44–0.78% and 0.00–2.15% respectively compared to the TDM values [33]. We note that \(\langle D,ns \rangle\) gives the largest deviation in the energy in our calculation, (2.15% for \(n=3\)) as well as the smallest deviation (0.00% for \(n=8\)). However it is also noted that significantly varied and contrasting excitation energies were reported in the literature for this resonance state, thus requiring more extensive and elaborate computations to determine its position with greater confidence. Recently accurate excitation energies corresponding to the higher resonances of both the series (\(n\) up to 22 and 25 for the former and latter series respectively) have been reported in the eigenphase derivative theory coupled with the R-matrix method, and the present results show absolute discrepancies in the range of 0.46–0.50% and 0.04–0.58% for the two series.

Next in table III we turn into a comparison of the calculated density functional results for the even- and odd-parity quartet P states arising from the 2p\(^2\)ns \(\langle C,ns \rangle\), \(n=2-24\) and 2s2pns \(\langle B,ns \rangle\), \(n=3-22\) with the available literature data. Experimental results are yet to be obtained for any of these states, while from a theoretical viewpoint, these are relatively less explored compared to the previously discussed hollow states. The energy of the lowest state of the even series in our calculation is only 0.004 a.u., above the CCR result [23], while the same for the odd series is only 0.0037 a.u., below the hyperspherical coordinate result [35] indicating the accuracy in the present method. Both these resonances have been reported through R-matrix calculation for \(n\) up to 9 [28] as well as in the TDM calculation for \(n\) up to 12 [33] and the current results show excellent agreement with both of these. The \(\langle B,ns \rangle\) series show overestimations in energies for all \(n\) compared to the TDM result [33], but the \(\langle C,ns \rangle\) series show underestimations as well for some of the states. For the moderately
TABLE II: Comparison of the state (in a.u.) and excitation energies (in eV) relative to the Li ground state [54], of 2s\(^2\)nd and 2p\(^2\)ns \(^2\)D\(^e\) resonances of Li. PW signifies present work.

| n  | \(-E(\text{a.u.})\) (A,\(n_d\) \(^2\)D\(^e\)) | Excitation energy(eV) | \(-E(\text{a.u.})\) (D,\(n_s\) \(^2\)D\(^e\)) | Excitation energy(eV) |
|----|-------------------------------------------------|-----------------------|-----------------------------------------------|-----------------------|
| 2  | 1.9461, 1.9614\(^a\), 1.9659\(^b\) | 150.512                | 149.826\(^d\), 150.095\(^b\), 149.982\(^f\) | 1.8458, 1.8489\(^e\), 1.8069\(^b\) |
| 3  | 1.9202, 1.9319\(^b\) | 151.216                | 150.484\(^d\), 150.898\(^b\), 150.651\(^f\) | 1.7955, 1.7782\(^b\) |
| 4  | 1.9100, 1.9193\(^b\) | 151.494                | 150.798\(^d\), 151.241\(^b\), 150.965\(^f\) | 1.7765, 1.7694\(^b\) |
| 5  | 1.9035, 1.9120\(^b\) | 151.671                | 150.968\(^d\), 151.439\(^b\), 151.137\(^f\) | 1.7672, 1.7645\(^b\) |
| 6  | 1.8945, 1.9084\(^b\) | 151.780                | 151.069\(^d\), 151.537\(^b\), 151.239\(^f\) | 1.7618, 1.7607\(^b\) |
| 7  | 1.8969, 1.9059\(^d\) | 151.850                | 151.141\(^d\), 151.605\(^b\), 151.312\(^f\) | 1.7586, 1.7586\(^b\) |
| 8  | 1.8951, 1.9042\(^d\) | 151.899                | 151.185\(^d\), 151.652\(^b\), 151.356\(^f\) | 1.7564, 1.7571\(^b\) |
| 9  | 1.8936, 1.9029\(^b\) | 151.940                | 151.217\(^d\), 151.687\(^b\) | 1.7549, 155.714, 155.065\(^d\) |
| 10 | 1.8924, 1.9020\(^b\) | 151.973                | 151.241\(^d\), 151.712\(^b\) | 1.7538, 155.744, 155.102\(^d\) |
| 11 | 1.8914                  | 152.000                | 151.260\(^d\) | 1.7530, 155.765, 155.122\(^d\) |
| 12 | 1.8906                  | 152.022                | 151.274\(^d\) | 1.7524, 155.782, 155.138\(^d\) |
| 13 | 1.8891                  | 152.035                | 151.285\(^d\) | 1.7519, 155.795, 155.151\(^d\) |
| 14 | 1.8897                  | 152.046                | 151.294\(^d\) | 1.7515, 155.806, 155.161\(^d\) |
| 15 | 1.8893                  | 152.057                | 151.302\(^d\) | 1.7512, 155.814, 155.169\(^d\) |
| 16 | 1.8890                  | 152.065                | 151.308\(^d\) | 1.7509, 155.823, 155.176\(^d\) |
| 17 | 1.8888                  | 152.071                | 151.313\(^d\) | 1.7507, 155.828, 155.182\(^d\) |
| 18 | 1.8886                  | 152.076                | 151.317\(^d\) | 1.7505, 155.833, 155.187\(^d\) |
| 19 | 1.8884                  | 152.082                | 151.321\(^d\) | 1.7504, 155.836, 155.191\(^d\) |
| 20 | 1.8883                  | 152.084                | 151.324\(^d\) | 1.7502, 155.842, 155.194\(^d\) |
| 21 | 1.8882                  | 152.087                | 151.327\(^d\) | 1.7501, 155.844, 155.197\(^d\) |
| 22 | 1.8881                  | 152.090                | 1.7500, 155.847, 155.200\(^d\) |
| 23 | 1.8880                  | 152.094                | 1.7499, 155.850, 155.202\(^d\) |
| 24 | 1.7498                  | 155.853                | 155.205\(^d\) |
| 25 | 1.7498                  | 155.853                | 155.205\(^d\) |

\(^a\)Reference [35].
\(^b\)Reference [33].
\(^c\)Reference [25].
\(^d\)Reference [31].
\(^e\)Reference [23].
\(^f\)Reference [28].
\(^g\)Reference [11].
TABLE III: Comparison of the state (in a.u.) and excitation energies (in eV) relative to the Li ground state [54], of 2p\(^2\)ns \(^4\)P\(^e\) and 2s2pns \(^4\)P\(^o\) resonances of Li. PW signifies present work.

| n | \(\langle C,ns \rangle \) \(^4\)P\(^e\) \(-E(\text{a.u.})\) | \(\langle B,ns \rangle \) \(^4\)P\(^o\) \(-E(\text{a.u.})\) | Excitation energy(eV) | PW | Ref. | Excitation energy(eV) | PW | Ref. |
|---|---|---|---|---|---|---|---|---|
| 2 | 2.2390 | 2.2394\(^a\), 2.2331\(^b\) | 142.543 | 142.533\(^a\), 142.59\(^c\), 142.703\(^b\) | 1.9878 | 1.9841\(^d\), \(^b\) | 149.377 | 149.478\(^d\), 149.409\(^c\) |
| 3 | 1.8838 | 1.8889\(^d\), \(^b\) | 152.207 | 152.068\(^a\), 151.976\(^c\) | 1.9312 | 1.9228\(^b\) | 150.917 | 151.146\(^b\), 151.045\(^c\) |
| 4 | 1.8127 | 1.8131\(^b\) | 154.141 | 154.130\(^b\), 153.892\(^c\) | 1.9108 | 1.8992\(^b\) | 151.472 | 151.788\(^b\), 151.619\(^c\) |
| 5 | 1.8033 | 1.8034\(^b\) | 154.397 | 154.394\(^b\), 154.147\(^c\) | 1.9011 | 1.8890\(^b\) | 151.736 | 152.065\(^b\), 151.889\(^c\) |
| 6 | 1.7979 | 1.7980\(^b\) | 154.544 | 154.541\(^b\), 154.290\(^c\) | 1.8956 | 1.8834\(^b\) | 151.886 | 152.218\(^b\), 152.039\(^c\) |
| 7 | 1.7947 | 1.7947\(^b\) | 154.631 | 154.631\(^b\), 154.378\(^c\) | 1.8922 | 1.8800\(^b\) | 151.978 | 152.310\(^b\), 152.131\(^c\) |
| 8 | 1.7925 | 1.7927\(^b\) | 154.691 | 154.685\(^b\), 154.436\(^c\) | 1.8899 | 1.8778\(^b\) | 152.041 | 152.370\(^b\), 152.191\(^c\) |
| 9 | 1.7909 | 1.7909\(^b\) | 154.734 | 154.734\(^b\) | 1.8884 | 1.8762\(^b\) | 152.082 | 152.413\(^b\) |
| 10 | 1.7898 | 1.7899\(^b\) | 154.764 | 154.761\(^b\) | 1.8873 | 1.8751\(^b\) | 152.111 | 152.443\(^b\) |
| 11 | 1.7890 | 1.7891\(^b\) | 154.786 | 154.783\(^b\) | 1.8864 | 1.8743\(^b\) | 152.136 | 152.465\(^b\) |
| 12 | 1.7884 | | 154.802 | | 1.8858 | | 152.152 | |
| 13 | 1.7879 | | 154.816 | | 1.8853 | | 152.166 | |
| 14 | 1.7875 | | 154.827 | | 1.8849 | | 152.177 | |
| 15 | 1.7872 | | 154.835 | | 1.8846 | | 152.185 | |
| 16 | 1.7869 | | 154.843 | | 1.8843 | | 152.193 | |
| 17 | 1.7867 | | 154.849 | | 1.8841 | | 152.199 | |
| 18 | 1.7865 | | 154.854 | | 1.8839 | | 152.204 | |
| 19 | 1.7864 | | 154.857 | | 1.8838 | | 152.207 | |
| 20 | 1.7862 | | 154.862 | | 1.8836 | | 152.212 | |
| 21 | 1.7861 | | 154.865 | | 1.8835 | | 152.215 | |
| 22 | 1.7860 | | 154.868 | | | | |
| 23 | 1.7859 | | 154.870 | | | | |

\(^a\)Reference [23].
\(^b\)Reference [33].
\(^c\)Reference [28].
\(^d\)Reference [35].

For high-lying \(\langle C,ns \rangle\) states with \(n\geq6\), we notice almost complete agreement in the energies in our calculation with the TDM values [33]. The calculated energies for the even- and odd-parity states are 0.00–0.27% and 0.19–0.65% above and below the TDM values for up to the 12th resonance respectively. The deviations in the excitation energies are 0.03–0.17% and 0.02–0.10% for the two series relative to the R-matrix results [28]. Resonances above \(n=12\) are reported here for the first time for both these series.

The even- and odd-parity 2s2pnp \(\langle B,np \rangle\), \(n=3\)–22 and 2p\(^2\)np \(\langle C,np \rangle\), \(n=3\)–20 \(^4\)D hollow
resonances of Li are calculated and compared in Table IV. No experimental results have been reported as yet for any of these states, and the theoretical results are quite scanty. The calculated lowest state energies of the two series are 0.23% and 0.02% below both the hyperspherical [35] as well as TDM results [33] respectively. The density functional state energies for the even-parity resonances (up to \( n \leq 12 \)) match well with the TDM values with overestimations in the range of 0.23–0.65%, whereas the same of the odd-parity states match excellently (both overestimations and underestimations are noticed) with those having deviations from 0.006–0.02%. The discrepancies in the calculated excitation energies remain within 0.04–0.10% and 0.11–0.17% for the even- and odd-parity states with respect to the R-matrix values [28]. The excitation energies up to the 12th resonance for both the series, calculated using the TDM calculation [33] are also quoted in the table and the present results show satisfactory agreement. No reference results are found in the literature for the resonances with \( n \geq 13 \).

Table V now compares the computed state- and excitation energies for the \( 2s2pnd \ (C,nd) \ 4F^o, n=3–20 \) and \( 2p^2nd \ (B,nd) \ 4F^e, n=3–24 \) hollow resonances of Li with the existing literature data. Once again, no experimental results are yet available for these resonances and very few theoretical results have been reported so far. The calculated lowest state energies of the two series show good agreement with the hyperspherical [35] as well as the TDM [33] energies having absolute deviations 0.19% and 0.23% respectively; the former is overestimated, while the latter underestimated. The overall agreements in the state energies with respect to the TDM results for the former and latter resonances are good (overestimations by 0.19–0.46%) and excellent (underestimations by 0.02–0.23%) respectively for \( n \) up to 11 and 12 respectively. The excitation energies match quite decently with the R-matrix results [28] having absolute deviations in the ranges 0.03–0.04% and 0.16–0.19% (for resonances up to 9) as well as with the TDM values [33]. Resonances with \( n > 12 \) for both of these series are calculated here for the first time.

Finally table VI computes and compares the last of the \( 2l'2l''n'' \) hollow resonance series of Li considered in this work, viz., \( 2p^2np \ (D,np) \ 2F^o, n=3–23 \) and \( 2p^2nd \ (D,nd) \ 2G^e, n=3–22 \) respectively. Once again experimental results are as yet unavailable for both of these series. No theoretical results are reported for the latter series, whereas the same for the former series is quite scarce. The present computed term energy of the lowest \( 2F^o \) resonance is in good agreement with the hyperspherical [35] as well as the TDM [33] calculations (underestimated

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TABLE IV: Comparison of the state (in a.u.) and excitation energies (in eV) relative to the Li ground state [54], of 2s2pnp \(^4\)D\(^e\) and 2p\(^2\)np \(^4\)D\(^o\) resonances of Li. PW signifies present work.

| n   | \(-\left\langle B, np \right\rangle \) \(^4\)D\(^e\) | Excitation energy(eV) | \(-\left\langle C, np \right\rangle \) \(^4\)D\(^o\) | Excitation energy(eV) |
|-----|--------------------------------------------------|-----------------------|--------------------------------------------------|-----------------------|
|     | PW Ref.                                           | PW Ref.               | PW Ref.                                           | PW Ref.               |
| 3   | 1.9705                                           | 1.9659\(^a,b\)       | 149.848                                           | 149.973\(^b\),149.907\(^c\) |
| 4   | 1.9251                                           | 1.9168\(^b\)         | 151.083                                           | 151.309\(^b\),151.197\(^c\) |
| 5   | 1.9081                                           | 1.8969\(^b\)         | 151.546                                           | 151.850\(^b\),151.685\(^c\) |
| 6   | 1.8996                                           | 1.8877\(^b\)         | 151.777                                           | 152.101\(^b\),151.924\(^c\) |
| 7   | 1.8947                                           | 1.8826\(^b\)         | 151.910                                           | 152.239\(^b\),152.060\(^c\) |
| 8   | 1.8916                                           | 1.8795\(^b\)         | 151.994                                           | 152.324\(^b\),152.145\(^c\) |
| 9   | 1.8896                                           | 1.8774\(^b\)         | 152.049                                           | 152.381\(^b\),152.201\(^c\) |
| 10  | 1.8881                                           | 1.8760\(^b\)         | 152.090                                           | 152.419\(^b\)         |
| 11  | 1.8871                                           | 1.8749\(^b\)         | 152.117                                           | 152.449\(^b\)         |
| 12  | 1.8863                                           | 1.8741\(^b\)         | 152.139                                           | 152.471\(^b\)         |
| 13  | 1.8857                                           | 1.8755               | 152.155                                           | 152.783               |
| 14  | 1.8852                                           | 1.8769               | 152.169                                           | 152.787               |
| 15  | 1.8848                                           | 1.8774               | 152.179                                           | 152.829               |
| 16  | 1.8845                                           | 1.8781               | 152.188                                           | 152.838               |
| 17  | 1.8843                                           | 1.8769               | 152.193                                           | 152.843               |
| 18  | 1.8841                                           | 1.8767               | 152.199                                           | 152.849               |
| 19  | 1.8840                                           | 1.8766               | 152.201                                           | 152.851               |
| 20  | 1.8839                                           | 1.8765               | 152.204                                           | 152.854               |
| 21  | 1.8838                                           | 152.207              |
| 22  | 1.8837                                           | 152.209              |

\(^{a}\)Reference [35].

\(^{b}\)Reference [33].

\(^{c}\)Reference [28].

by 0.42%). The state energies remain above by 0.14–0.46% from the TDM values [33] and the absolute deviations in excitation energies are 0.28–0.35% with respect to the R-matrix results [28].

As a further extension of the present method, table VII gives results for several higher lying triply excited hollow resonances of Li in which both the K and L shells are empty, the so-called doubly hollow states, \(3l'\l''n''(3 \leq \l' \leq 6)\) (\(2\)S\(^e\), \(2\)P\(^o\), \(2\)D\(^e\), \(2\)F\(^o\), \(4\)S\(^o\), \(4\)P\(^e,o\), \(4\)D\(^e,o\) and \(4\)F\(^o\)\). Although a decent number of accurate, reliable experimental and theoretical results are available for the \(2l'2\l''n''\) resonances of Li as already discussed in tables I through VI, the same for resonances having all the three electrons residing in shells with principal quantum numbers 3 or more, are very limited presumably because of the greater challenges.
TABLE V: Comparison of the state (in a.u.) and excitation energies (in eV) relative to the Li ground state [54], of 2s2pnd 4F₀ and 2p²nd 4Fₑ resonances of Li. PW signifies present work.

| n  | (C,nd) 4F₀ | (B,nd) 4Fₑ |
|----|----------|----------|
|    | -E(a.u.) | Excitation energy(eV) | -E(a.u.) | Excitation energy(eV) |
| PW | Ref. | PW | Ref. | PW | Ref. | PW | Ref. |
| 3  | 1.9397  | 1.9360a,b | 150.686 | 150.786b,150.723c | 1.8456  | 1.8498a,b | 153.246 | 153.132b,153.004c |
| 4  | 1.9128  | 1.9061b | 151.418 | 151.600b,151.465c | 1.8181  | 1.8215b | 153.994 | 153.902b,153.705c |
| 5  | 1.9010  | 1.8925b | 151.739 | 151.970b,151.807c | 1.8070  | 1.8081b | 154.296 | 154.266b,154.045c |
| 6  | 1.8940  | 1.8854b | 151.929 | 152.163b,151.991c | 1.8002  | 1.8009b | 154.481 | 154.462b,154.229c |
| 7  | 1.8898  | 1.8812b | 152.043 | 152.277b,152.101c | 1.7961  | 1.7966b | 154.593 | 154.579b,154.339c |
| 8  | 1.8871  | 1.8786b | 152.117 | 152.348b,152.171c | 1.7935  | 1.7939b | 154.664 | 154.653b,154.410c |
| 9  | 1.8853  | 1.8768b | 152.166 | 152.397b,152.210c | 1.7916  | 1.7921b | 154.715 | 154.702b,154.458c |
| 10 | 1.8840  | 1.8755b | 152.201 | 152.433b | 1.7904  | 1.7907b | 154.748 | 154.740b |
| 11 | 1.8830  | 1.8746b | 152.228 | 152.457b | 1.7894  | 1.7898b | 154.764 | 154.764b |
| 12 | 1.8822  | | 152.250 | | 1.7887  | 1.7890b | 154.794 | 154.786b |
| 13 | 1.8816  | | 152.267 | | 1.7881  | | 154.810 |
| 14 | 1.8811  | | 152.280 | | 1.7877  | | 154.821 |
| 15 | 1.8807  | | 152.291 | | 1.7873  | | 154.832 |
| 16 | 1.8804  | | 152.299 | | 1.7871  | | 154.838 |
| 17 | 1.8802  | | 152.305 | | 1.7868  | | 154.846 |
| 18 | 1.8800  | | 152.310 | | 1.7866  | | 154.851 |
| 19 | 1.8799  | | 152.313 | | 1.7864  | | 154.857 |
| 20 | 1.8798  | | 152.316 | | 1.7863  | | 154.859 |
| 21 |         | | 1.7862  | | 154.862 |
| 22 |         | | 1.7861  | | 154.865 |
| 23 |         | | 1.7860  | | 154.868 |
| 24 |         | | 1.7859  | | 154.870 |

*a*Reference [35].

*b*Reference [33].

*c*Reference [28].

encountered. Some distinctive features of these resonances are: they are weak (by about an order of magnitude compared to the previously discussed hollow states), broad and having much larger widths [8]. The principal difficulties in dealing with such higher hollow states at larger photon energies are mainly due to a very rapid increase in the density of possible triply excited states and the lower states of same symmetry, as well as of the number of open channels available, leading to very strong and quite complicated electron correlation effects. In the CCR calculation, this might require cumbersome construction and diagonalization of complex matrices of very large order to search for the behavior of a great number of roots in the complex energy plane. On the other hand, in a FD type
TABLE VI: Comparison of the state (in a.u.) and excitation energies (in eV) relative to the Li ground state [54], of $2p^2np\ ^2F^o$ and $2p^2nd\ ^2G^e$ resonances of Li. PW signifies present work.

| n   | $-\langle D, np\rangle$ | $\langle D, nd\rangle$ | $-\langle D, np\rangle$ | $\langle D, nd\rangle$ |
|-----|-------------------------|------------------------|-------------------------|------------------------|
| PW  | Ref.                    | PW                     | Ref.                    | PW                     |
| 3   | 1.8429                  | 1.8506$^{a,b}$         | 153.319                 | 153.110$^b$,152.892$^c$|
| 4   | 1.7908                  | 1.7991$^b$             | 154.737                 | 154.511$^b$,154.240$^c$|
| 5   | 1.7743                  | 1.7787$^b$             | 155.186                 | 155.066$^b$,154.651$^c$|
| 6   | 1.7660                  | 1.7686$^b$             | 155.412                 | 155.341$^b$,154.921$^c$|
| 7   | 1.7611                  | 1.7636$^b$             | 155.545                 | 155.477$^b$,155.039$^c$|
| 8   | 1.7581                  | 1.7608$^b$             | 155.627                 | 155.553$^b$,155.117$^c$|
| 9   | 1.7561                  |                        | 155.681                 | 155.185$^c$            |
| 10  | 1.7545                  | 1.7583$^b$             | 155.725                 | 155.621$^b$            |
| 11  | 1.7536                  | 1.7569$^b$             | 155.749                 | 155.659$^b$            |
| 12  | 1.7529                  |                        | 155.768                 |                        |
| 13  | 1.7523                  |                        | 155.784                 |                        |
| 14  | 1.7518                  |                        | 155.798                 |                        |
| 15  | 1.7514                  |                        | 155.809                 |                        |
| 16  | 1.7511                  |                        | 155.817                 |                        |
| 17  | 1.7509                  |                        | 155.823                 |                        |
| 18  | 1.7507                  |                        | 155.828                 |                        |
| 19  | 1.7505                  |                        | 155.833                 |                        |
| 20  | 1.7503                  |                        | 155.839                 |                        |
| 21  | 1.7502                  |                        | 155.842                 |                        |
| 22  | 1.7501                  |                        | 155.844                 |                        |
| 23  | 1.7500                  |                        | 155.847                 |                        |

$^a$Reference [35].
$^b$Reference [33].
$^c$Reference [28].

For example, the energies and decay rates of N$^{4+}$ and N$^{2+}3l^33l^\prime 3l^\prime\prime$ configurations using a CI approach [22]; positions and widths of N$^{4+}$ (3,3,3) $^2S_e,o$ states employing the space partition as well as a stabilization procedure both of which use the L$^2$ discretization [26]; large scale state specific theory calculations for 11 n=3 resonances of He$^-$ accounting for all localized electron correlations [21]; critical issues in the theory and computation of the lowest three n=3 intrashell states, viz., 3s$^23p\ ^2P^o$, 3s3p$^2\ ^4P^e$ and 3s3p$^2\ ^2D^e$ of Z=2–7 in the light of state specific theory [55]; energies, widths and Auger branching ratios for eight He$^-$ $3l^33l^\prime 3l^\prime\prime$ states.
using the CCR method [55], etc. A semiquantitative analysis of the angular correlation of 64 n=3 intrashell states of a model three-electron atom confined on the surface of a sphere were presented recently [57]. The only triply photoexcited (3,3,3) KL-hollow states studied so far for Li are the 3s^23p^2 2P_0 and 3s3p^2 4P_e, both theoretically whereas only the former experimentally. Synchrotron radiation measurement [8] and photoion spectroscopy [13] give its position at 175.25 eV and 175.165±0.050 eV respectively. Theoretically, a 570-term 25 angular component wave function gives an energy of −1.043414 a.u., and the position at 174.11 eV, in an SP calculation with R-matrix approximation [13], which agrees quite well with the recent CCR result of −1.043 a.u., involving correlated basis sets [53], and the state specific result [55] of −1.0409856 a.u., as well as with the the multiconfiguration Dirac-Fock [8] excitation energy of 174.14 eV. Our energy value of −1.01210 a.u., gives its position at 175.940 eV, which is about 0.67 eV above the experimental value of [8] and matches well with the state specific result of 175.15 eV [55]. Our calculated state energy of −1.02288 a.u., for the latter matches closely with the state specific result of −1.0393859 a.u. [55]. No other results are available for any of these states for further comparison and these results may be useful in future studies of these resonances. It may be noted that the present result gives 3s3p^2 4P_e as the lowest n=3 resonance rather than the 3s^23p^2 2P_0, the former lying 0.0108 a.u., below the latter. This ordering is in keeping with the CCR findings of [56] for He as well as that of the CI calculation for N^{4+} [22]. However it differs from that of [55], who find in a large scale state specific calculation that as in the n=2 resonances, the 3s^23p^2 2P_0 lies below 3s3p^2 4P_e for Li isoelectronic series, mainly because of the localized electron correlation; the separation for Li being about 0.0016 a.u. Clearly, better correlation functionals would be required to achieve such smaller separations (of the order of 1×10^{-3} a.u.) within this DFT formalism. Now Fig. 1 depicts the radial densities for some representative (a) 2l2l'nl'' and (b) 3l3l'nl'' hollow states and show the characteristic shell structures (superpositions of the orbital radial densities).

At this stage it is worthwhile to make a few pertinent remarks on the status of excited state calculations within DFT. Although founded in the 1920s and later rejuvenated in the 1960s in the works of Hohenberg, Kohn and Sham [58,59], DFT has been a very powerful and successful tool for the electronic structure calculation of atoms, molecules, solids in their ground states [60,61], inherent difficulties were encountered for the excited states and consequently in areas such as spectroscopy, its success has been relatively less conspicuous.
TABLE VII: Calculated term energies (in a.u.) and excitation energies (in eV) of Li relative to the ground state [54], of some selected 3l3l’nl” states.

| State          | −E   | Exc. energy | State          | −E   | Exc. energy | State          | −E   | Exc. energy |
|----------------|------|-------------|----------------|------|-------------|----------------|------|-------------|
| 3s²4s 2S        | 0.90054 | 178.959     | 3p³ 4S         | 1.00055 | 176.238     | 3p²4s 2P        | 0.89600 | 179.012     |
| 3s²5s 2S        | 0.87011 | 179.787     | 3p³ 2D         | 0.90847 | 177.111     | 3p²5s 4P        | 0.86978 | 179.796     |
| 3s²6s 2S        | 0.85729 | 180.136     | 3s3p4s 4P      | 0.93313 | 178.072     | 3p²6s 4P        | 0.85744 | 180.132     |
| 3s²3p 2P        | 1.01210 | 175.924a,c  | 3s3p5s 4P      | 0.90193 | 178.921     | 3p²4s 2D        | 0.87282 | 179.713     |
| 3s²4p 2P        | 0.89129 | 179.211     | 3s3p6s 4P      | 0.88901 | 179.273     | 3p²5s 2D        | 0.84534 | 180.461     |
| 3s²5p 2P        | 0.86656 | 179.883     | 3s3p4p 4D      | 0.92678 | 178.245     | 3p²6s 2D        | 0.83330 | 180.788     |
| 3s²6p 2P        | 0.85558 | 180.182     | 3s3p5p 4D      | 0.89924 | 178.994     | 3p²4p 4D        | 0.89642 | 179.071     |
| 3s²3d 2D        | 0.97108 | 177.040     | 3s3p6p 4D      | 0.88767 | 179.309     | 3p²5p 4D        | 0.86846 | 179.832     |
| 3s²4d 2D        | 0.88088 | 179.494     | 3s3p3d 4F      | 1.02643 | 175.534     | 3p²6p 4D        | 0.85669 | 180.152     |
| 3s²5d 2D        | 0.86240 | 179.997     | 3s3p4d 4F      | 0.91125 | 178.667     | 3p²4p 2F        | 0.86932 | 179.808     |
| 3s²6d 2D        | 0.85352 | 180.238     | 3s3p5d 4F      | 0.89400 | 179.137     | 3p²5p 2F        | 0.84343 | 180.513     |
| 3s³2p 24P       | 1.02288 | 175.630     | 3s3p6d 4F      | 0.88517 | 179.377     | 3p²6p 2F        | 0.83225 | 180.817     |
| 3s³2p 2D        | 0.99479 | 176.394     |                |       |             |                |       |             |

*Reference theoretical values are: 1.043414 a.u. [13], 1.043 a.u. [53] and 1.040985 a.u. [55].
*bReference experimental results are: 175.25 eV [8] and 175.165±0.050 eV [13].
*cReference theoretical values are: 174.11 eV [13], 174.14 eV [8] and 175.15 eV [55].
*dReference theoretical value is: 1.0393859 a.u. [55].

The well-known fundamental problems such as the lack of a unique exact formal relationship valid for general excited states parallel to the KS method for ground states, as well as the unavailability of hitherto unfound universal XC energy density functional etc., have been well documented in the literature in considerable length (see, for example, [43] for a review). Nevertheless, numerous attractive and elegant formalisms have been suggested by many authors over the years; e.g., the subspace formulation of DFT [62] and its application to atomic excited states [63], ensemble formalism for the unequally weighted states using a Rayleigh-Ritz variational principle [64], a perturbative treatment [65,66], calculation of multiplet energies within the Hartree-Fock-Slater method utilizing the spin-polarized form of the density matrix and exploiting Slater’s sum rule [52,67,68], ensemble approach using several appropriate functionals [69,70], the time-dependent (TD) DFT formulation [71-73] making use of the TD DF response theory, etc. Recently correlation energies of several atomic excited states were calculated using the MCSCF wave functions [74]. While some of these methods offer good quality results, others produce large errors and yet others are computationally difficult to implement. Moreover most of these methods have dealt with the lower and singly excited states; multiple and higher excitations, especially the
Rydberg series such as the ones studied in this work, have not been reported so far using any other DFT approach except the work-function formalism. Besides, while some of these methods, such as TDDFT, provides a way to obtain excitation energies in an efficient and accurate manner (calculates the linear response of the system to a TD perturbation, leading to frequency dependent dynamic dipole polarizability, whose poles and residues yield the excitation energies and oscillator strengths respectively), the extraction of individual state energies as well as the densities, are not straightforward. In the present method however, the energies, excitation energies as well the densities and expectation values are obtained easily with reasonable accuracy. To the best of our knowledge, this is the first report of triply excited Rydberg resonances of many-electron systems within a DFT-based formalism. We also note that the spin polarized version of the work-function exchange potential can be obtained as a further approximation to the accurate spin polarized X-only KS potential (obtained from a consideration of the optimized effective potential method) [75]. Various interesting features of the method may be found in the references [27,38-44].

IV. CONCLUDING REMARKS

Twelve triply excited 2l2l′nl′′ hollow Rydberg series of Li (covering a total of about 270 states) have been studied using a density functional approach. Nonrelativistic term
energies, excitation energies and radial densities are reported for both low as well as higher members (up to n=25) of these odd- and even-parity resonances. The GPS solution of the KS type equation yields results in fairly good agreement with the existing literature data. Additionally 37 $3l'{}^3nl''$ hollow states are also presented in the photon energy range 175.63–180.51 eV, out of which only two ($3s^23p^2\,^2P^o$ and $3s3p^2\,^4P^e$) have been reported so far in the literature. The resonance series interact with each other resulting in very complicated behavior in their positions. Many new resonances are reported here for the first time.

The combination of work-function exchange and the LYP correlation functional within an essentially single determinantal framework offers results quite comparable in accuracy with those from other sophisticated and elaborate quantum mechanical methods. The exchange-only results are practically of HF-quality; a feature of the work-function formalism observed in a number of physical systems including atoms, ions, metals, etc., (see, for example [76,77]). Consequently, since these are strongly correlated systems, one of the main sources of error in this calculation could be due to the inefficiency of the LYP functional to incorporate the subtle and intricate correlation effects, which may be either improved or replaced by more accurate density functionals. However, this may not be misconstrued as a drawback of the methodology; in fact the results are rather quite encouraging, especially in the light of DFT’s apparent weaknesses and lack of any density-based attempts as yet for these Rydberg series. The assumption of spherical symmetry in calculating the exchange potential, might be the another possible cause of inaccuracy. Thus the rotational component of the electric field may not have negligible contribution compared to the irrotational component for these states, although for atoms this usually holds true [49]. The extension of this prescription to even higher photon-energy hollow states such as the case where all three electrons remain in shells with $n\geq4$, i.e., the KLM vacancy states etc., are straightforward, as well as its application to positive and negative ionic systems and extension to the relativistic domain. It may also be interesting to employ some of the other DFT-based approaches to treat these and other similar systems, so that the nature of the intricate electron correlation may be understood better. Some works in these directions are under progress.
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