Density functional studies on the hollow resonances in the Li-isoelectronic sequence (Z = 4–10)

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Abstract
Following from our work on triply excited hollow resonances in three-electron atomic systems, a density functional theory (DFT)-based formalism is employed to investigate similar resonances in the Li-isoelectronic series (Z = 4–10). A combination of the work-function-based local nonvariational exchange potential and the popular gradient plus Laplacian-included Lee–Yang–Parr correlation energy functional is used. The generalized pseudospectral method provides nonuniform and optimal spatial discretization of the radial Kohn–Sham equation. First, all the eight n = 2 intrashell states of B²⁺, N⁴⁺ and F⁶⁺ are presented, which are relatively less studied in the literature compared to the remaining four members. Then calculations are performed for the eight 2l 2l′ 2n 2l′′ (3 ⩽ n ⩽ 6) hollow resonance series, namely 2s²ns 2S⁰, 2s²np 2P⁰, 2s²nd 2D⁰, 2s²pns 2P⁰, 2s²pnp 2D⁰, 2p²ns 4P⁰, 2p²np 4D⁰ and 2p²ns 2D⁰, of all the seven positive ions. Next, as an illustration, higher resonance positions of the 2s²ns 2S⁰ series are calculated for all the ions with a maximum of n = 25. The calculated excitation energies are in excellent agreement with the available literature data (for the n = 2 intrashell states the deviation is within 0.125% and excepting only one case, the same for the resonance series is well below 0.5%). With an increase in Z, the deviations tend to decrease. Radial densities are also presented for some of the selected states. The only result available in the literature for the lower resonances (corresponding to a maximum of n = 17) have been reported very recently. The n > 16 (17 for F⁶⁺) resonances are examined here for the first time. This gives a promising viable and general DFT scheme for the accurate calculation of these and other hollow resonances in many-electron atoms.

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1. Introduction

With all three electrons residing in $n \geq 2$ shells leaving the K shell empty, the three-electron atomic system constitutes an interesting multi-excited atomic problem. These are ideal for examining the delicate interelectronic correlation of three electrons under the influence of a nucleus, the well-known four-body Coulombic problem. A large majority of these triply excited hollow states are autoionizing and have found important practical applications in the field of high-temperature dense plasma diagnostics using high-resolution x-ray spectroscopy [1]. Ever since their first observation in an electron–helium scattering experiment by Kuyatt et al [2] and the same for Li and some of the highly charged ions in beam-foil experiments [3–5], many subsequent attempts were made to study the spectra of these challenging systems over the past three decades. However, the lowest $2s^2 2p^2 \; ^2P^0$ resonance of Li in a photoabsorption experiment was reported by Kiernan et al [6] only in 1994 with the aid of a dual-laser plasma technique. In recent years, continuing impressive developments in the synchrotron radiation technology has spawned a great upsurge of interest to measure the position, width and lifetime of these hollow atomic and ionic resonances with greater accuracy and precision. Some of these include, for example, but not limited to, the measurement of (a) the various even- and odd-parity hollow resonances using photoelectron, photoion spectroscopy [7–11], (b) the photoionization cross section [12], (c) the Rydberg series [13] as well as (d) both K and L shell vacancy states, the so-called doubly hollow states [8, 14], etc.

From a theoretical perspective, due to the presence of strong and subtle electron correlation effects as well as an infinite number of open channels associated with these resonances, accurate and dependable calculation of their energies and widths have posed formidable difficulties to the theoreticians. This in addition with the availability of numerous powerful and sophisticated quantum mechanical formalisms have stimulated an extensive amount of theoretical works in the recent years. In one of the earliest attempts, Ahmed and Lipsky [15] calculated the lowest triply excited resonances of Li-like atoms by a configuration-interaction (CI)-type formalism. In a later work, Safronova and Senashenko [16] performed a detailed and systematic study on the $n=2$ intrashell states of the Li-isoelectronic series employing a $1/Z$ expansion approach for a wide range of $Z$. Thereafter, a multitude of theoretical methodologies have been proposed which provide results in fairly good agreement with the experimental works, namely, the joint saddle point (SP) and complex coordinate rotation (CCR) method [17–20], the state-specific theory [21, 22], the space partition and stabilization approach [23], the $R$-matrix theory along with many of its variants [24, 25], the truncated diagonalization method (TDM) [26–28], the hyperspherical coordinate formalism [29, 30], etc.

While a number of formally attractive and elegant methodologies are now available within the traditional wavefunction based framework, attempts within a density functional viewpoint have been surprisingly very rare. The latter can be advantageous and desirable in the sense that the former often requires large basis sets and also usually a significant mixing of the continuum states. Also whereas a substantial amount of experimental and theoretical results exist for Li, only a few theoretical studies [19–21, 23, 27, 28, 31–35] have been made so far. Although remarkable progress has been achieved lately for similar resonances of some systems including highly charged ions as already mentioned, such resonances are yet to be observed for the Li-isoelectronic sequence, which would greatly enhance our understandings on these systems. Almost all the publications on these ions have dealt exclusively only with the $2l^2/2l^0$ intrashell states; the only reported results on the $2l^1nl''(n > 2)$ resonance series, such as those considered in this work, are due to the
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Density functional studies on the hollow resonances in the Li-isoelectronic sequence (Z = 4–10) [1593] recent TDM tabulations of Conneely et al [27, 28]. Besides, to the best of my knowledge, we are not aware of any density-based results so far for the hollow resonances of these three-electron ions. The objective of this paper is therefore to provide results for such spectra in the lesser explored domain of the Li-isoelectronic series using a density functional theory (DFT)-based approach with an aim to judge the performance of this formalism in comparison to the commonly used wavefunction-based methodologies in the literature. Earlier an attempt was made to calculate all the eight n = 2 intrashell triply excited states of the Li-isoelectronic series (Z = 2–4, 6, 8, 10) [36] with reasonably good accuracy within the purview of nonrelativistic Hohenberg–Kohn–Sham (HKS) DFT. In this scheme, a local nonvariational work-function-based exchange potential [37] and the nonlinear correlation energy functional of Lee–Yang–Parr (LYP) [38] containing the gradient and Laplacian of the density was utilized. The resulting KS-type differential equation was numerically solved in the usual self-consistent manner exploiting the Numerov-type finite difference (FD) scheme. Within a single-determinantal approach, this has been shown to deliver fairly accurate results for various multiply excited states of closed- and open-shell many-electron atoms and ions, e.g., the low and high as well as the valence and core excitations, bound and autoionizing states, the satellite states, etc ([39–44], and the references therein). However, because of the Coulomb singularity at r = 0 and the long-range −1/r behaviour, the FD schemes for the radial discretization often requires significantly larger number of grid points to achieve reasonable accuracy even for the ground states and are therefore not feasible for the high-lying Rydberg states. To circumvent this problem, subsequently a generalized pseudospectral (GPS) technique was suggested for the numerical solution of the KS equation for purposes of greater accuracy and efficiency [45]. Recently, the GPS method has been applied quite successfully in the context of electronic structure and dynamics calculation of the Coulombic singularities in atoms, molecules, as well as other systems, such as the spiked harmonic oscillators with stronger singularities, the logarithmic potentials, etc [45–50]. Using this GPS implementation, the singly excited state energies for He, and Li and Be were calculated within 0.01% and 0.02% compared to the best available literature data; while the doubly excited states of He deviated by a maximum of 3.60%. Furthermore, the calculated single and double excitation energies were within the ranges of 0.009–0.632% and 0.085–1.600%, respectively. This provided the motivation to apply this procedure to the more complicated and arguably more interesting triply excited hollow resonance series of the three-electron atoms and ions. The validity and usefulness of this formalism has been amply demonstrated in a recent study [51] on the 12 2l′2l′′nl” (n ⩾ 2) hollow resonance series of Li covering a total of about 270 low- and high-lying states (with a maximum of n = 25). The excited state energies were found to remain well within 0.98% (with one exception) whereas the excitation energies showed discrepancies in the range of 0.021%–0.058%. Additionally, 37 3l′3l′′nl” (n ⩾ 3) doubly hollow states were reported, most of them for the first time ever.

Here, we first compare the DFT excitation energies for all the eight 2l′2l′′nl” triply excited states, namely 2s2 2p 4Po, 2s2p2 2D, 4P, 2P, 2S; and 2p3 5D, 2P, 4S of some selected members of the Li-isoelectronic series, namely B+, N++, and F++. Then we focus on the eight even- and odd-parity doublet and quartet 2l′′nl” (3 ⩽ n ⩽ 6) hollow resonance series, namely, 2s2ns 3S, 2s2np 3P, 2s2nd 3D, 2s2pns 4P, 2s2ppn 4D, 2p2ns 4P, 2p2np 4D and 2p2ns 4D, of all the members in the series (Z = 4–10). In all the cases, comparisons with the available experimental and other theoretical results have been made, wherever possible. The paper is organized as follows: section 2 summarizes the basic formalism as well as the computational strategy. Section 3 gives a discussion of the computed results while a few concluding remarks are presented in section 4.
2. Methodology

The calculation of atomic excited states within the work-function formalism [39–44, 36] and its GPS implementation [45, 51] has been presented in detail previously and will not be repeated here. In the following therefore we present only a brief overview of it while addressing the essential problems associated with the excited state DFT and some recent developments in this direction. Atomic units are used throughout the paper unless otherwise mentioned.

Ever since the formal inception in the works of Hohenberg–Kohn–Sham [52, 53] nearly four decades ago, DFT has emerged as a powerful practical tool for studying the ground-state properties of many-electron systems such as atoms, molecules, solids, etc. This is chiefly due to its ability to incorporate the electron correlation effects in a clever and computationally inexpensive way. However, inherent difficulties were recognized almost immediately for excited state calculations for the following reasons. No Hohenberg–Kohn like theorem exists for a general excited state as the wavefunction cannot be bypassed through the pure-state density in this case. This is easily realizable from the hydrodynamic formulation [54] of the wavefunction; the phase part of the hydrodynamic function is not constant for a general excited state, although the constancy remains valid for the ground and some static stationary excited states. In other words, the complex-valued wavefunction cannot be replaced by the real pure-state density function alone and hence both the charge and current densities have to be taken into consideration. Also an accurate (not to speak of the exact) functional form of the exchange-correlation (XC) energy in terms of the density (incorporating the symmetry dependence) is as yet unknown and may not necessarily have the same dependence on density as for the ground states. Thus although it is advantageous to work in terms of density for the ground states, it is not possible to characterize an individual excited state completely in terms of density (angular momentum quantum numbers are required to classify them). Despite all these problems, a variety of promising and appealing formalisms have been proposed in the past years and this continues to remain a very fertile and demanding area of research. Some of the notable ones are, for example, (a) the subspace formulation of DFT [55] invoking the concept of ensemble density instead of the pure-state density, (b) a constrained search method [56] bypassing the Hohenberg–Kohn theorem while defining the functionals in terms of the Slater determinants, (c) several variants of the ensemble density approach [57, 58] employing several different forms of the approximate functionals, (d) a Rayleigh–Ritz-type variational principle of unequally weighted ensemble [59], (e) a time-dependent (TD) formulation of DFT for excited states [60–62], based on the TD density functional response theory, (f) a perturbative treatment [63, 64], where the non-interacting KS Hamiltonian corresponds to the zeroth-order Hamiltonian and the differences in the KS eigenvalues simply give the zeroth-order excitation energies. Recently, multiplet energies for transition metal atoms and ions with 3dⁿ configurations have been reported [65] using the SCF KS orbitals to construct the atomic multiplet determinantal combinations.

Despite all these attempts, a general prescription that can yield the bound and resonance states of a many-electron system reliably and accurately in a simple and uniform way for both low and high excitations would be highly desirable. This is partly because, although some of the above methods produce good-quality results for certain states, cause significantly large errors for other states making them unsuitable, presumably due to the fact that the potentials used are the ones obtained for the ground states and also importantly lacking the correct asymptotic behaviour. Some others are difficult to implement computationally. Furthermore, applications have been mostly restricted to the single excitations and low-lying states; results for double, triple or other multiple excitations as well as for higher lying states like the Rydberg series studied here, have been very scant [45, 51]. The work-function formulation of
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excited states as used in this work, either bypasses or partly overcomes the above-mentioned problems of DFT in dealing with the excited states via an amalgamation of the conventional wavefunction based quantum mechanics within DFT such that the atomic orbital and the electronic configuration features are retained and we summarize its essential features below.

The point of central interest is the following KS-type differential equation of the form:

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

(1)

In this equation, \( v_{es}(\mathbf{r}) \) signifies the usual Hartree electrostatic potential including the electron–nuclear attraction and the interelectronic Coulomb repulsion,

\[
v_{es}(\mathbf{r}) = -\frac{Z}{r} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}'
\]

(2)

while \( v_{xc}(\mathbf{r}) \), the total XC potential is partitioned as

\[
v_{xc}(\mathbf{r}) = v_x(\mathbf{r}) + v_c(\mathbf{r}).
\]

(3)

Now making the assumption that a unique exchange potential exists for a given excited state, one can physically interpret it as the work done to move an electron against the electric field \( E_x(\mathbf{r}) \) arising out of the Fermi-hole charge distribution, \( \rho_x(\mathbf{r}, \mathbf{r}') \), which can be expressed by the following line integral:

\[
v_x(\mathbf{r}) = -\int_\infty^\mathbf{r}' E_x(\mathbf{r}) \cdot d\mathbf{l}.
\]

(4)

where the field \( E_x(\mathbf{r}) \) has the following form:

\[
E_x(\mathbf{r}) = \int \frac{\rho_x(\mathbf{r}, \mathbf{r}') (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}'.
\]

(5)

In order that the potential is well defined, the work done must be path independent (irrotational) and this is rigorously the case for spherically symmetric systems. This work against \( E_x(\mathbf{r}) \) can be determined exactly as the Fermi hole is known explicitly in terms of the single-particle orbitals:

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

(6)

where

\[
\gamma(\mathbf{r}, \mathbf{r}') = \sum_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}')
\]

(7)

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 \( \phi_i(\mathbf{r}) = R_{nl}(\mathbf{r}) Y_{l m}(\Omega) \), give the total electron density as the sum of the occupied orbitals,

\[
\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2.
\]

At this point, we note that the usual DFT route of obtaining the potential as a functional derivative is avoided by introducing the physical interpretation that the dynamic Fermi–Coulomb hole charge determines the potential. The exchange potential does not have an explicit density functional form (unlike the usual practice in DFT) and it is universal; the electronic configuration of a particular state defines it so that the same KS equation is now equally valid for both ground and excited states. Although this formalism is in the spirit of Slater’s interpretation of exchange energy based on the notion of Fermi hole, this is expected to offer better results compared to the HFS scheme as it incorporates the dynamic nature of
the charge distribution. The asymptotic behaviour of the fully correlated potential (both \( v_x(r) \) and \( v_c(r) \)) is that of \( v_x(r) \) only and falls off as \(-1/r\) for atomic systems. However although this path allows an accurate determination of \( v_x(r) \) as elaborated, an analogous procedure leading to the accurate form of \( v_c(r) \) valid for a general excited state is as yet unknown, because the Coulomb hole is not known explicitly in terms of orbitals and therefore requires to be approximated. Several approximate forms have been proposed in the literature ever since DFT’s inception; this work uses the well-known LYP [38] functional which has been found to be quite a good choice for the problem at hand. With this choice of \( v_x(r) \) and \( v_c(r) \), the KS equation is solved numerically to obtain the self-consistent set of orbitals and the densities therefrom. Because \( v_x(r) \) is local, the solution of the resultant KS equation is computationally much easier than the HF case. From this set of orbitals, various Slater determinants are constructed and different multiplet energies corresponding to a particular electronic configuration are calculated by following Slater’s diagonal sum rule [66], earlier employed within the context of DFT in [67]. Numerous other aspects of this formalism can be found in [39–45, 36, 51].

Now a few words about the GPS discretization technique is in order. The commonly used equal-spacing FD schemes often require a significantly large number of spatial grid points because of the Coulomb singularity as well as the long-range nature of these physical systems; even for the accurate calculation of their ground states. The present Legendre pseudospectral discretization approach alleviates this uncomfortable feature in our calculation in three steps: (a) the semi-infinite domain \( r \in [0, \infty) \) is mapped onto the finite domain \( x \in [-1, 1] \) by the transformation \( r = r(x) \), (b) then an algebraic nonlinear mapping [68, 69] is used, followed by a (c) symmetrization procedure leading to a set of coupled equations. The overall process gives rise to a symmetric matrix eigenvalue problem which can be accurately and easily solved to yield the eigenvalues and eigenfunctions by using the standard routines. This allows therefore nonuniform and optimal discretization, maintaining similar accuracies at both small (denser mesh) and large (coarser mesh) \( r \) regions with a significantly smaller number of grid points with the promise of a fast convergence. We used a consistent convergence criteria of \( 10^{-6} \) and \( 10^{-8} \) au, for the potential and eigenvalues, respectively; while a maximum of 500 radial grid points proved to be sufficient to achieve convergence for all the states reported in this work.

3. Results and discussion

At first we present the computed density functional results for the nonrelativistic ground-state energies (in au) of the Li-isoelectronic series, namely Be\(^{+}\), B\(^{2+}\), C\(^{3+}\), N\(^{4+}\), O\(^{5+}\), F\(^{6+}\) and Ne\(^{7+}\) ions in table 1. These are compared with the three best theoretical results in the literature, namely the fully correlated Hylleraas-type variational method [70], the full core plus correlation using multiconfiguration-interaction wavefunctions [71] and large expansion of the Hylleraas-type functions [72, 73]. Our results show fairly good agreement with all of these. Slight overestimation is observed in the range of 0.0016% for Be\(^{+}\) to 0.0002% for Ne\(^{7+}\). Here we note that within the variationally founded HKS DFT, all many-body interactions are incorporated into the local multiplicative potential \( \delta E_{xc}[\rho]/\delta \rho \), whose exact form remains unknown as yet. As stated earlier, the current formalism is not derived from the variational principle for energy. As a result, even though a KS-type equation is solved to obtain the energies and densities, the total procedure is not subject to a variational bound.

Table 2 displays the computed nonrelativistic excitation energies in eV (1 au = 27.207 6544 eV) of all the eight triply excited states arising from electronic configurations 2s\(^2\) 2p, 2s2p\(^2\) and 2p\(^3\) of the ions B\(^{2+}\), N\(^{4+}\) and F\(^{6+}\). We have chosen these three ions partly because the work-function results have been previously reported (albeit within a different numerical
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### Table 1. Comparison of the calculated nonrelativistic ground-state energies (in au) of the Li-isoelectronic series, \(Z = 4–10\) with the literature data. PW signifies present work.

| \(Z\) | Energy | PW | Reference |
|-------|--------|-----|-----------|
| 4     | \(-14.324\) | \(-14.324\) 763\(^a\), \(-14.324\) 761\(^b\), \(-14.324\) 760\(^c\) |
| 5     | \(-23.424\) | \(-23.424\) 605\(^d\), \(-23.424\) 604\(^e\), \(-23.424\) 603\(^f\) |
| 6     | \(-34.775\) | \(-34.775\) 511\(^g\), \(-34.775\) 508\(^h\), \(-34.775\) 509\(^i\) |
| 7     | \(-48.377\) | \(-48.376\) 898\(^j\), \(-48.376\) 896\(^k\), \(-48.376\) 895\(^l\) |
| 8     | \(-64.228\) | \(-64.228\) 542\(^m\), \(-64.228\) 539\(^n\), \(-64.228\) 538\(^o\) |
| 9     | \(-82.330\) | \(-82.330\) 338\(^p\), \(-82.330\) 337\(^q\), \(-82.330\) 336\(^r\) |
| 10    | \(-102.682\) | \(-102.682\) 231\(^s\), \(-102.682\) 228\(^t\), \(-102.682\) 229\(^u\) |

\(^a\) Reference [70].
\(^b\) Reference [71].
\(^c\) Reference [72].
\(^d\) Reference [73].

### Table 2. Comparison of the calculated excitation energies (in eV) of the \(n = 2\) intrashell triply excited states of \(B^{2+}, N^{4+}\) and \(F^{6+}\) relative to the nonrelativistic ground states of [70]. PW signifies present work.

| State     | \(B^{2+}\) | \(N^{4+}\) | \(F^{6+}\) |
|-----------|-------------|-------------|-------------|
| \(2s^2 2p^2 \ 3p^0\) | 436.588 | 436.07\(^a\), 436.59\(^b\) | 894.541 | 893.93\(^a\), 894.12\(^b\) |
| \(2s^2p^2 \ 4p^0\) | 436.917 | 436.69\(^a\), 436.89\(^b\) | 894.876 | 894.54\(^a\), 894.51\(^b\) |
| \(2s^2p^2 \ 2D^e\) | 441.893 | 441.34\(^a\), 442.00\(^b\) | 902.655 | 901.93\(^a\), 902.32\(^b\) |
| \(2p^3 \ 4S^o\) | 443.852 | 443.86\(^a\), 444.13\(^b\) | 905.329 | 905.15\(^a\), 905.15\(^b\), 904.43\(^d\) |
| \(2s^2p^2 \ 2P^e\) | 445.387 | 445.11\(^a\), 445.75\(^b\) | 907.930 | 907.41\(^a\), 907.87\(^b\) |
| \(2s^2p^2 \ 2P^o\) | 445.814 | 445.35\(^a\), 446.21\(^b\) | 908.455 | 907.99\(^a\), 908.59\(^b\) |
| \(2p^3 \ 2D^s\) | 446.173 | 446.02\(^a\), 446.58\(^b\) | 909.089 | 909.02\(^a\), 909.37\(^b\) |
| \(2p^3 \ 3p^0\) | 450.088 | 450.04\(^a\), 450.65\(^b\) | 915.023 | 915.00\(^a\), 915.47\(^d\) |

\(^a\) Reference [31].
\(^b\) Reference [27].
\(^c\) Reference [28].
\(^d\) Reference [74].

procedure) for the even-\(Z\) series as well as for \(He^-\) and \(Li\) [36]; so we do not repeat them. Besides in the literature, relatively less results are available for the odd-\(Z\) series [27, 28, 31, 74] than the even-\(Z\) series [19–21, 27, 28, 31, 74]. Therefore it may be useful to have the results for the odd-\(Z\) series, which will complete the work-function results for the isoelectronic series up to \(Z = 10\). Also in this work, our primary focus in on the \(2l2l'nl''\) \((n > 2)\) resonance series. It is worth mentioning here that in our previous work on the hollow resonances in \(Li\) [51], the excited state energies were also presented in addition to the excitation energies. Throughout this work however, we no longer report the state energies to avoid too many entries in the tables and also because that the available reference values of these state energies for direct comparison are quite scarce. For a proper comparison, our density functional excitation energies presented in this and all other tables are estimated relative to the respective accurate nonrelativistic ground states of these ions of [70]. No experimental results can be found for these states as yet and only a few theoretical studies have been made. The \(2p^1 \ 4S^o\) states of these ions are bound, metastable against autoionization by conservation of parity and angular momentum and were reported by using a multiconfiguration-interaction-type formalism within...
Table 3. Calculated excitation energies (in eV) of various triply excited states of Be+, B2+, and C3+ relative to the nonrelativistic ground states of [70]. PW signifies present work and the TDM values are quoted from [27].

| State | Be+ | B2+ | C3+ |
|-------|-----|-----|-----|
|       | PW  | TDM | PW  | TDM | PW  | TDM |
| ⟨A, 3s⟩ 2Se | 285.924 | 284.694 | 285.904 | 284.684 | 286.017 | 285.692 |
| ⟨A, 4s⟩ 2Se | 290.424 | 289.192 | 290.407 | 289.184 | 290.822 | 290.407 |
| ⟨A, 5s⟩ 2Se | 293.118 | 292.103 | 293.098 | 292.091 | 293.417 | 293.098 |
| ⟨A, 6s⟩ 2Se | 293.221 | 292.111 | 293.216 | 292.108 | 293.540 | 293.116 |
| ⟨A, 3p⟩ 2Po | 287.034 | 285.418 | 287.019 | 285.411 | 287.434 | 285.919 |
| ⟨A, 4p⟩ 2Po | 290.827 | 289.570 | 290.812 | 289.563 | 291.242 | 290.812 |
| ⟨A, 5p⟩ 2Po | 292.405 | 291.325 | 292.391 | 291.312 | 292.778 | 292.391 |
| ⟨A, 6p⟩ 2Po | 293.221 | 292.111 | 293.206 | 292.098 | 293.616 | 293.206 |
| ⟨A, 3d⟩ 2De | 288.563 | 287.355 | 288.550 | 287.343 | 288.975 | 288.550 |
| ⟨A, 4d⟩ 2De | 291.371 | 290.144 | 291.356 | 290.137 | 291.777 | 291.356 |
| ⟨A, 5d⟩ 2De | 292.672 | 291.556 | 292.651 | 291.543 | 293.095 | 292.651 |
| ⟨A, 6d⟩ 2De | 293.221 | 292.111 | 293.206 | 292.098 | 293.616 | 293.206 |
| ⟨B, 3s⟩ 4Po | 285.331 | 285.508 | 285.326 | 285.501 | 285.758 | 285.326 |
| ⟨B, 4s⟩ 4Po | 289.867 | 290.468 | 290.454 | 290.447 | 290.894 | 290.454 |
| ⟨B, 5s⟩ 4Po | 291.662 | 292.152 | 291.648 | 292.141 | 292.100 | 291.648 |
| ⟨B, 6s⟩ 4Po | 292.566 | 293.058 | 292.552 | 293.045 | 293.491 | 292.552 |
| ⟨B, 3p⟩ 4De | 286.120 | 286.400 | 286.105 | 286.389 | 286.537 | 286.105 |
| ⟨B, 4p⟩ 4De | 290.169 | 290.495 | 290.154 | 290.447 | 290.645 | 290.154 |
| ⟨B, 5p⟩ 4De | 291.804 | 292.318 | 291.789 | 292.272 | 292.628 | 291.789 |
| ⟨B, 6p⟩ 4De | 292.642 | 293.148 | 292.627 | 293.080 | 293.436 | 292.627 |
| ⟨C, 3s⟩ 4Pe | 288.792 | 289.284 | 288.777 | 289.270 | 289.625 | 289.270 |
| ⟨C, 4s⟩ 4Pe | 293.058 | 293.567 | 293.043 | 293.536 | 293.891 | 293.536 |
| ⟨C, 5s⟩ 4Pe | 294.788 | 295.417 | 294.773 | 295.390 | 295.746 | 295.390 |
| ⟨C, 6s⟩ 4Pe | 295.667 | 296.288 | 295.652 | 296.265 | 296.620 | 296.265 |
| ⟨C, 3p⟩ 4Do | 289.483 | 290.011 | 289.468 | 290.004 | 289.821 | 290.004 |
| ⟨C, 4p⟩ 4Do | 293.477 | 293.833 | 293.462 | 293.816 | 294.190 | 293.816 |
| ⟨C, 5p⟩ 4Do | 295.099 | 294.545 | 295.085 | 294.538 | 295.452 | 294.538 |
| ⟨C, 6p⟩ 4Do | 295.926 | 296.358 | 295.911 | 296.345 | 296.698 | 296.345 |
| ⟨D, 3s⟩ 2De | 290.710 | 290.264 | 290.695 | 290.258 | 291.065 | 290.258 |
| ⟨D, 4s⟩ 2De | 294.857 | 294.982 | 294.847 | 294.974 | 295.320 | 294.974 |
| ⟨D, 5s⟩ 2De | 296.557 | 296.979 | 296.551 | 296.958 | 297.125 | 296.958 |
| ⟨D, 6s⟩ 2De | 297.425 | 297.868 | 297.419 | 297.857 | 298.092 | 297.857 |

a Rayleigh–Ritz variational principle [74]. Recently, the position of all these states for these ions have been calculated by Safronova and Bruch [31] on the basis of a perturbation theory method (1/Z expansion) as well as by Conneely et al [27, 28] following the TDM. It is evident that the current positions of these states for all the three ions follow the same rank orderings of [31] and [27, 28]. For all these states, excellent agreement with the literature data is noted with the largest absolute discrepancy of 0.125% (the deviation ranges are 0.0005–0.125%, 0.007–0.049% and 0.044–0.099% for the three ions, respectively). The present excitation energies for B2+ show underestimations for all but the 2s2p 2 4Pe state compared to [27] and overestimations for all but the 2p 3 4So state relative to [31]. N4+ gives overestimations for all the states relative to [31], while overestimations for all but the last three states with respect to [28]. F6+ excitation energies are underestimated for all the states compared to all the literature results. Note that excitation energies of [27, 28] and [74] are quoted here with respect to the same ground states of [70].
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Table 4. Calculated excitation energies (in eV) of various triply excited 2l2l′nl′′ (3 \( \leq n \leq 6 \)) resonances of N4+, O5+, F6+ and Ne7+ relative to the nonrelativistic ground states of [70]. PW signifies present work and the TDM values are taken from [28].

| State          | N4+    | O5+    | F6+    | Ne7+   |
|----------------|--------|--------|--------|--------|
|               | PW     | TDM    | PW     | TDM    |
| (A, 3s) 2s⁰   | 960.417| 959.883| 1274.141| 1274.141|
| (A, 4s) 2s⁰   | 981.845| 981.747| 1303.860| 1304.322|
| (A, 5s) 2s⁰   | 991.077| 990.786| 1316.797| 1316.911|
| (A, 6s) 2s⁰   | 995.903| 995.697| 1323.602| 1324.026|
| (A, 3p) 2p⁰   | 962.928| 961.437| 1277.093| 1275.961|
| (A, 4p) 2p⁰   | 982.814| 982.555| 1305.000| 1305.294|
| (A, 5p) 2p⁰   | 991.556| 991.398| 1317.360| 1317.714|
| (A, 6p) 2p⁰   | 996.184| 996.146| 1323.923| 1324.315|
| (A, 3d) 3d⁰   | 966.440| 966.089| 1281.261| 1281.495|
| (A, 4d) 3d⁰   | 984.120| 983.804| 1306.586| 1306.973|
| (A, 5d) 3d⁰   | 992.211| 991.907| 1318.168| 1318.441|
| (A, 6d) 3d⁰   | 996.570| 996.279| 1324.413| 1324.696|
| (B, 3s) 4p⁰   | 961.584| 961.336| 1276.318| 1275.798|
| (B, 4s) 4p⁰   | 983.089| 983.306| 1306.126| 1306.154|
| (B, 5s) 4p⁰   | 992.328| 992.696| 1319.074| 1319.249|
| (B, 6s) 4p⁰   | 997.410| 997.471| 1325.882| 1325.917|
| (B, 3p) 4d⁰   | 983.339| 983.409| 1287.410| 1287.268|
| (B, 4p) 4d⁰   | 997.837| 998.125| 1307.043| 1307.144|
| (B, 5p) 4d⁰   | 992.707| 993.093| 1319.553| 1319.722|
| (B, 6p) 4d⁰   | 997.378| 997.713| 1326.170| 1326.279|
| (C, 3s) 4p⁰   | 986.130| 986.685| 1283.917| 1284.333|
| (C, 4s) 4p⁰   | 988.982| 989.515| 1312.945| 1313.336|
| (C, 5s) 4p⁰   | 998.053| 998.600| 1325.691| 1326.034|
| (C, 6s) 4p⁰   | 1002.817| 1003.375| 1332.420| 1332.852|
| (C, 3p) 4d⁰   | 969.947| 970.570| 1286.183| 1286.597|
| (C, 4p) 4d⁰   | 990.223| 990.119| 1314.536| 1314.066|
| (C, 5p) 4d⁰   | 999.032| 998.221| 1326.970| 1326.399|
| (C, 6p) 4d⁰   | 1003.677| 1003.579| 1333.552| 1333.048|
| (D, 3s) 2d⁰   | 971.302| 971.765| 1287.366| 1288.082|
| (D, 4s) 2d⁰   | 991.863| 992.143| 1316.065| 1316.626|
| (D, 5s) 2d⁰   | 1000.861| 1001.816| 1328.720| 1329.822|
| (D, 6s) 2d⁰   | 1005.595| 1006.770| 1335.413| 1336.776|

Now we turn our focus on to the 2l2l′nl′′ (n \( \geq 3 \)) hollow resonance series. The excitation energies (in eV) for the eight such even- and odd-parity series, namely \((A, ns)^2s\), \((A, np)^2p^0\), \((A, nd)^2p^0\), \((B, ns)^4p^6\), \((B, np)^4d^2\), \((C, ns)^4p^4\), \((C, np)^4d^2\) and \((D, ns)^2D^2\) of the Li-like ions with Z = 4–10, relative to the same ground states [70] as used in table 2, are tabulated in tables 3 and 4, respectively. In these two tables we restrict ourselves to the lower resonances with \(3 \leq n \leq 6\), whereas the higher resonances are given later. The independent particle model classification of [26–28] has been utilized, i.e., these states are classified according to the Rydberg series which converge on each of the six lowest 2l2l′ doubly excited core states of the residual two-electron systems, namely 2s\(^2\) 1S\(\text{r}\), 2s2p \(^1\)P\(\text{r}\), 2p\(^2\) \(^1\)D\(\text{r}\), 2s2p \(^1\)P and 2p\(^2\) \(^1\)S\(\text{r}\), denoted by A, B, C, D, E and F, respectively. Again no experimental results can be found for any of these resonances and we are not aware of any other theoretical attempts except for the recent extensive TDM tabulations [27, 28]. We quote the TDM excitation energies relative to the same ground states of [70] as used for the present...
Table 5. Calculated excitation energies (in eV) of the 2s\(^n\) 2p\(^n\)Se\(^{(n=7–25)}\) resonances of the Li-isoelectronic series \((Z = 4–10)\) relative to the nonrelativistic ground states of [70]. PW signifies present work and the TDM values are quoted from [27, 28].

|    | Be\(^+\) | B\(^{2+}\) | C\(^{3+}\) | Ne\(^{4+}\) |
|----|---------|---------|---------|---------|
| \(n\) | PW      | TDM     | PW      | TDM     | PW      | TDM     |
| 7  | 293.635 | 292.636 | 481.761 | 480.770 | 716.794 | 716.117 |
| 8  | 293.959 | 292.900 | 482.452 | 481.486 | 717.980 | 717.311 |
| 9  | 294.176 | 293.107 | 482.917 | 481.927 | 718.780 | 718.100 |
| 10 | 294.329 | 293.249 | 483.243 | 482.240 | 719.346 | 718.644 |
| 11 | 294.440 | 293.368 | 483.483 | 482.446 | 719.762 | 719.069 |
| 12 | 294.522 | 293.447 | 483.662 | 482.694 | 720.075 | 719.363 |
| 13 | 294.587 | 293.510 | 483.801 | 482.822 | 720.318 | 719.599 |
| 14 | 294.636 | 293.561 | 483.910 | 482.941 | 720.508 | 719.795 |
| 15 | 294.677 | 483.999 | 483.018 | 720.663 | 719.942 | 1004.683 |
| 16 | 294.710 | 484.071 | 720.788 | 720.064 | 1004.877 |
| 17 | 294.737 | 484.130 | 720.892 | 1005.037 |
| 18 | 294.759 | 484.179 | 720.976 | 1005.170 |
| 19 | 294.778 | 484.220 | 721.049 | 1005.285 |
| 20 | 294.794 | 484.256 | 721.112 | 1005.380 |
| 21 | 294.808 | 484.286 | 721.166 | 1005.462 |
| 22 | 294.821 | 484.313 | 721.213 | 1005.532 |
| 23 | 294.832 | 484.334 | 721.251 | 1005.595 |
| 24 | 294.843 | 484.356 | 721.286 | 1005.649 |
| 25 | 294.851 | 484.373 | 721.319 | 1005.698 |

Calculations. At a first glance, the overall agreement of the density functional excitation energies with the reference values is quite gratifying. The largest absolute deviation is found to be 0.57% for the \(\langle A, 3p\rangle P^{2+}\) state of Be\(^+\); for all other cases, the same remains well below 0.5%. In three instances, our results completely match with the TDM values, e.g., the \(\langle A, 3s\rangle S^{2+}\) of O\(^{5+}\), \(\langle A, 3p\rangle P^{2+}\) and \(\langle C, 3s\rangle P^{4+}\) states of Ne\(^{7+}\). The absolute deviation ranges are 0.042–0.566%, 0.016–0.375%, 0.007–0.247%, 0.004–0.155%, 0.000–0.102%, 0.002–0.090% and 0.000–0.103% for \(Z = 4, 5, 6, 7, 8, 9\) and 10 ions, respectively. As in the previous table,
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Figure 1. The radial densities (au) of Be$^+$ for (a) 2s$^2$3p $^2$P$^o$, 2p$^2$3s $^2$D$^o$, 2s2p3s $^4$P$^o$ and (b) 2s$^2$3s $^2$S$^o$, 2s$^2$ 4s $^2$S$^o$.

Figure 2. The radial densities (au) of 2s$^2$3s $^2$S$^o$ states for (a) B$^2+$, C$^3+$, N$^4+$ and (b) O$^5+$, F$^6+$, Ne$^7+$ respectively.

here also we note both over- and under-estimations. Generally speaking, accuracy of our calculation increases with an increase in Z for a particular state. This is largely due to the fact that electrons are pulled closer to the nucleus with an increase in Z; the depth of the Coulomb potential increases and the one-electron contributions to the energy becomes more important than the correlation term (which is dealt with comparatively less accurately).

To further demonstrate the usefulness and applicability of the prescription, we now report in table 5 the excitation energies (relative to the same ground state of [70]) corresponding to the high-lying Rydberg states of the 2s$^2$ns $^2$S$^o$ ($n = 7$–25) hollow resonances for all the seven ionic species. To the best of my knowledge, no experimental observation has been made as of today and no other theoretical results exist for any of these resonances except the recent TDM calculations [27, 28], which are appropriately quoted. These reference results are available for resonances up to $n = 14, 15, 17$ for Be$^+$, B$^2+$, F$^6+$ and $n = 16$ for the remaining ions. The
present density functional excitation energies are overestimated for Be\(^+\), B\(^{2+}\), C\(^{3+}\), N\(^{4+}\) with mean absolute deviations 0.363\%, 0.205\%, 0.098\%, 0.028\%, respectively, while the same for O\(^{5+}\), F\(^{6+}\), Ne\(^{7+}\) show the opposite trend with the mean absolute deviations 0.020\%, 0.057\% and 0.080\%, respectively. Once again the deviations are larger for low \(Z\) and tends to diminish with an increase in \(Z\). As pointed out in several recent works for the hollow Rydberg series of Li including the present formalism [24–26, 51], these resonances are also expected to be highly entangled to each other, making their precise theoretical calculation as well as experimental observation significantly complicated. However, as expected, the separation between the successive members within a resonance series increases as \(Z\) goes up. The resonances above \(n = 17\) are reported in this work for the first time. At this stage, it is worthwhile to mention that although the TDM method is advantageous in the sense of obtaining the whole resonance series at once as well as enabling an accurate classification of the energy levels on the basis of configuration mixing and quantum defects in a uniform and consistent manner, the excitation energies are generally not as accurate as some of the other existing approaches (such as the saddle point method) [26–28]. Thus, more precise elaborate calculational and experimental results would be needed to resolve some of the discrepancies observed in this work as well as to unveil various interesting features associated with these resonances. Finally, in figure 1 we show the radial densities of Be\(^+\) for 2\(s^2\) 3\(p^2\) 3\(p^2\) 3\(s^2\) 2\(D^e\), 2\(s^2\)p\(^2\) 3\(s^2\) 4\(p^e\) in (a) and 2\(s^2\) 3\(s^2\) 2\(S^e\), 2\(s^2\) 4\(s^2\) 5\(S^e\) in (b) while figure 2 depicts the radial densities of 2\(s^2\) 3\(s^2\) 2\(S^e\) states for B\(^{2+}\), C\(^{3+}\), N\(^{4+}\) in (a) and for O\(^{5+}\), F\(^{6+}\), Ne\(^{7+}\) in (b), respectively. As expected, the peaks are shifted to smaller values of \(r\) as \(Z\) increases and of course the desired shell structure is observed in all these plots.

4. Conclusion

In this follow-up of our proposed density functional approach to the triply excited states [36] and its recent GPS extension to hollow resonance series in Li [51], a detailed and elaborate study has been made for the seven positive ions in the Li-isoelectronic sequence (\(Z = 4–10\)). The nonrelativistic excitation energies and radial densities were presented for both low and higher members in these odd- and even-parity Rydberg series with excellent accuracy. First, all the eight \(n = 2\) intrashell triply excited states, namely 2\(s^2\)2\(p^2\) 3\(p^e\), 2\(s^2\)p\(^2\) 3\(s^2\) 2\(D^e\), 2\(s^2\)p\(^2\) 3\(s^2\) 4\(p^e\), 2\(p^e\), 2\(S^e\); and 2\(p^3\) 2\(D^e\), 2\(P^o\), 4\(S^e\); of B\(^{2+}\), N\(^{4+}\) and F\(^{6+}\) were compared with the available literature data. Then we compared the calculated excitation energies of eight 2\(l/2\)\(n/2\) (3 \(\leq n \leq 6\) resonance series of all the ions with the only reference TDM result available so far in the literature. Finally, we singled out the 2\(s^2\) 3\(s^2\) 2\(S^e\) series to demonstrate the feasibility and viability of this formalism for the high-lying Rydberg series by calculating the latter for all members with \(n\) up to a maximum of 25. Literature results for these systems have been recently reported for a maximum \(n\) of 17 for F\(^{6+}\) (\(\leq 16\) for other ions) and thus all the resonances lying above are presented here for the first time. Out of about 380 states considered in this work, the excitation energies show a maximum absolute deviation of 0.57\% (for 2\(s^2\) 3\(p^2\) 3\(P^o\) state of Be\(^+\); excepting this lone case the latter remains below 0.5\%), which further consolidates the validity of the present density functional formalism in the domain of atomic excited states. Although a substantial amount of results are currently available for the higher resonances in Li, the same for the higher members of the isoelectronic sequence are very rare, and we hope that these results will provide helpful references in future theoretical and experimental works. Naturally more accurate theoretical calculations and experimental measurements would be required which could shed more light on our understanding of these triply excited resonances.

The use of local nonvariational work-function-based exchange potential and the nonlocal LYP correlation energy functional helps retaining the features of traditional wavefunction-based quantum mechanics within DFT that lies at the success of this approach. The
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nonuniform spatial GPS discretization of the pertinent KS-type equation in conjunction with the nonlinear mapping and the symmetrization procedure within an essentially single-determinantal framework offers results that are quite comparable in accuracy to other sophisticated and elaborate theoretical methodologies existing in the literature. Given the fact that these are strongly correlated systems, and the work-function exchange potential offers almost HF-quality results for ground and excited states of a variety of physical systems [44, 75, 76] including atoms, ions, metals etc, a major and obvious source of error in our work is the correlation energy functional, which is designed mainly for the ground states. While we are forced by the current inadequate status of DFT to use this potential, development of a universal prescription for the correlation potential, if possible, in the same spirit as the work-function exchange, would be highly desirable and challenging. Put differently, the correlation functional may be either improved or replaced to describe the intricate correlation effects in a transparent way leading to better accuracy. A secondary and lesser contributing source of inaccuracy may be due to the tacit assumption of spherical symmetry in the work-function exchange. Here, we note that a consideration of the optimized effective potential method leads to the work-function exchange potential as a further approximation to the accurate spin-polarized X-only KS potential [77]. Lately this potential has been used considerably for excited state DFT calculations of molecular systems within TDDFT, and it would be very desirable to exploit its accurate short- and long-range nature for these strongly correlated systems. The extension of this method to other hollow resonances, as well to higher photon-energy hollow series where all the three electrons reside in the shells with $n \geq 4$, is equally straightforward and simple. In conclusion, this work emphasizes the applicability and feasibility of a simple general and efficient DFT-based formalism for accurate and reliable calculation of the hollow resonances in multiply excited atomic systems.

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