Photoelectron momentum distribution of ground- and excited-state lithium atoms induced by extreme-ultraviolet photon absorption


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Abstract

We perform a theoretical investigation of the photoelectron momentum distribution (PMD) after ionization of a lithium (Li) atom, initially prepared in the ground (1s\textsuperscript{2}2s) or excited (1s\textsuperscript{2}2p) state, by extreme ultraviolet (XUV) radiation of frequency 85 eV that was previously measured in an experiment with the free-electron laser in Hamburg (2009 Phys. Rev. Lett. \textbf{103} 103008). The experiment revealed three distinct peaks in PMD with absolute momentum values of 2.4, 1.2 and 0.8 atomic units (a.u.), respectively. We carry out an all-electron calculation based on time-dependent density functional theory (TDDFT) and find that the two outer PMD peaks (2.4 and 1.2 a.u.) are well described by the single ionization from the valence (2s) and core (1s) electron shells, while the innermost peak (0.8 a.u.) is not reproduced. However, the peak at this position is found in the TDDFT calculation of a Li\textsuperscript{+} ion (1s\textsuperscript{2}) subject to the same XUV radiation, thus the TDDFT calculations are in good agreement with the experimental measurements if one assumes that the innermost peak originates from a Li\textsuperscript{+} ion rather than a neutral atom. We estimate possible production of Li\textsuperscript{+} ions by the pumping infrared laser used in the experiment to prepare the target atoms in the 1s\textsuperscript{2}2p excited state prior to interaction with the XUV field.

Keywords: strong field physics, photoelectron momentum distribution, time-dependent density functional theory, lithium atom

(Some figures may appear in colour only in the online journal)

1. Introduction

A lithium (Li) atom presents a unique problem in multi-electron strong-field physics. It is the simplest open-shell system where its outermost electron orbital is partially filled, so that its energy and time evolution depend on spins [1–9]. In 2009, Zhu \textit{et al} [10] measured the photoelectron momentum distribution (PMD) of Li atoms driven by an extreme ultra violet (XUV) pulse produced at the free-electron laser in Hamburg (FLASH). They used a magneto-optical trap and an optical pumping laser whose frequency is locked to the Li 1s\textsuperscript{2}2s \rightarrow Li\textsuperscript{2+} 1s\textsuperscript{2}2p transition frequency (670 nm) to prepare an excited p-state prior to the XUV irradiation, as shown in figure 1, and compared the resulting PMD with the ground-state PMD. Their state-of-art reaction microscope provided unprecedented momentum resolutions, around a few percent...
of an atomic unit [11]. While their results for double-ionization have been theoretically investigated intensively based on the close-coupling methods [12–15] or the two-electron TDSE [16], their Li-atom PMDs associated with single ionization have not. In this paper, we would like to address the origin of three distinct photoelectron momenta in a single-ionization event [10] in coincidence with Li\(^+\) ions (and therefore associated with single ionization) are directly related to the stationary-state orbital energies of a Li atom. Our calculations agree with their experiment in that an ionization yield of the valence electron is reduced when the initial state is prepared into an excited-state, compared to when it is in the ground state. However, contrary to the experiment, we do not observe the third transition spectrum attributed by Zhu et al to an ionization-excitation channel, which is a correlation effect and likely beyond the predictability of adiabatic approximation we adopt in our calculation. Yet a separate calculation with a Li\(^+\) ion as an initial state does predict the same photoelectron momentum as the third, innermost peak of the single-ionization PMD of a Li atom measured by Zhu et al; this suggests a possibility that the 670-nm optical pumping laser had produced Li\(^+\) ions (1s\(^5\)s) alongside the excited state, so that the resulting PMD would reflect the ionization potentials of both a Li atom and a Li\(^+\) ion.

We present an all-electron calculation of the PMDs of a Li atom driven by an XUV (85 eV) laser pulse, in accordance with Zhu et al’s experiment. Our calculation is based on time-dependent density functional theory (TDDFT) in the limit of the adiabatic approximation [18] and on Volkov-wave propagation of the released electrons at large distances from the atomic core [19]. The adiabatic approximation assumes that the exchange-correlation energies or potentials have the functional forms that come from the time-independent density functional theory but are evaluated with the time-dependent electron densities at the same time moment as the Kohn–Sham orbitals, i.e., no memory terms are included in the functional. The adiabatic approximation in TDDFT was previously tested in many time-dependent problems and proved fairly good for single excitation and ionization processes. Even for double ionization of the helium atom, the adiabatic exchange-correlation potential provides surprisingly accurate results [20]. For the Li atom, it was shown [9] that the adiabatic approximation works well even in the near-resonance Rabi-flopping regime.

The calculation of PMDs of a multi-electron wavefunction based on TDDFT is not a well-established subject, as its read-out functional in terms of electron density is unknown, but Kohn–Sham momentum distributions can be taken as an approximation [21]. Our previous TDDFT calculation of PMDs successfully produced the same features as measured during resonant two-color, two-photon ionization of helium and neon atoms [22]. TDDFT of an open-shell system such as a Li atom is more complicated than noble-gas atoms because electrons of opposite spins do not have the same Hamiltonian. We discuss our numerical scheme based on the local density approximation with self-interaction correction (LDA-SIC) [23, 24] and how it can be applied to an open-shell system. Moreover, in order to calculate the PMD of an excited-state Li atom, we evolve three electrons in an excited-state configuration (1s\(^3\)2p), whose eigenstates and eigenvalues are different from those in the ground-state configuration (1s\(^2\)2s). Development of such excited-state TDDFT is urgently needed since experiments with excited-state Li atoms are rapidly progressing in recent years [25, 26].

We find that two of the three ionization pathways observed by Zhu et al [10] in coincidence with Li\(^+\) ions (and therefore associated with single ionization) are directly related to the stationary-state orbital energies of a Li atom. Our calculations agree with their experiment in that an ionization yield of the valence electron is reduced when the initial state is prepared into an excited-state, compared to when it is in the ground state. However, contrary to the experiment, we do not observe the third transition spectrum attributed by Zhu et al to an ionization-excitation channel, which is a correlation effect and likely beyond the predictability of adiabatic approximation we adopt in our calculation. Yet a separate calculation with a Li\(^+\) ion as an initial state does predict the same photoelectron momentum as the third, innermost peak of the single-ionization PMD of a Li atom measured by Zhu et al; this suggests a possibility that the 670-nm optical pumping laser had produced Li\(^+\) ions (1s\(^5\)s) alongside the excited state, so that the resulting PMD would reflect the ionization potentials of both a Li atom and a Li\(^+\) ion.

The paper is organized as follows. In section 2, we describe our numerical methods to calculate PMDs of a state-prepared Li atom. First, the initial value problem is discussed in section 2.1. We examine various functionals for exchange-correlation potentials in section 2.2 to find which one in particular is suitable for TDDFT of an open-shell system such as a Li atom. Then, section 2.3 explains the time-evolution scheme of Kohn–Sham equations. Results are presented in section 3, and section 4 concludes our study. Atomic units (\(\epsilon = m_e = \hbar = 1\)) are used throughout, unless specified otherwise.
2. Methods

2.1. Initial value problem

Initial states of a Li atom are found by solving a set of three Kohn–Sham equations [27]

$$\mathcal{H}_0 \psi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma} \psi_{i\sigma}(\mathbf{r}) \quad (i = 1, 2, \ldots, N_e; \quad \sigma \in \{\uparrow, \downarrow\}),$$

(1)

where \(N_{\uparrow} = 2\) and \(N_{\downarrow} = 1\). The stationary Hamiltonian is given by

$$\mathcal{H}_0 = -\frac{1}{2} \nabla^2 - \frac{Z}{r} + v_{KS}[n_i, n_i](\mathbf{r}),$$

(2)

with \(Z = 3\). The electron–electron interaction potential \(v_{KS}[n_i, n_i](\mathbf{r})\) is a functional of up- and down-spin electron densities

$$n_{\sigma}(\mathbf{r}) = \sum_{i=1}^{N_{\sigma}} n_{i\sigma}(\mathbf{r}) = \sum_{i=1}^{N_{\sigma}} |\psi_{i\sigma}(\mathbf{r})|^2,$$

(3)

and it consists of two parts, such that

$$v_{KS}[n_i, n_i](\mathbf{r}) = V_H[n_i](\mathbf{r}) + v_{xc}[n_i, n_i](\mathbf{r}).$$

(4)

The first term in equation (4) is the Hartree potential

$$V_H[n_i](\mathbf{r}) = \int \frac{n(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d^3\mathbf{r'},$$

(5)

which is a functional of total electron density: \(n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r})\). The last term \(v_{xc}[n_i, n_i]\) in equation (4) is called the exchange-correlation potential and defined as the functional derivative of the exchange-correlation energy \(E_{xc}[n_i, n_i]\), i.e.,

$$v_{xc}[n_i, n_i](\mathbf{r}) = \frac{\delta E_{xc}[n_i, n_i]}{\delta n_{\sigma}(\mathbf{r})}.$$  

(6)

The exact functional for \(E_{xc}[n_i, n_i]\) is unknown and must be approximated in practice.

The total energy of the system is given by

$$E = T[n_i, n_i] + U[n] + J[n],$$

(7)

where \(T[n_i, n_i]\) is the non-interacting kinetic energy

$$T[n_i, n_i] = \sum_{i=1}^{N_i} \sum_{i=1}^{N_i} \int \psi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2\right) \psi_{i\sigma}(\mathbf{r}) d^3\mathbf{r},$$

(8)

\(U[n]\) is the Coulomb energy

$$U[n] = \int \left(-\frac{Z}{r}\right) n(\mathbf{r}) d^3\mathbf{r},$$

(9)

and \(J[n]\) is the Hartree energy

$$J[n] = \frac{1}{2} \int V_H[n](\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}.$$  

(10)

The total energy can also be found as

$$E = \sum_{\sigma} \varepsilon_{i\sigma} - J[n] - U_{ec}[n] + E_{xc}[n_i, n_i],$$

(11)

where

$$U_{ec}[n] = \sum_{\sigma} \int d^3\mathbf{r} \ v_{ec}^{\sigma}[n_i, n_i](\mathbf{r}) n_{\sigma}(\mathbf{r}).$$

(12)

The Kohn–Sham equations (1) are solved self-consistently using the generalized pseudospectral (GPS) method [28]. For an asymptotic condition, we impose

$$v_{xc}^{\sigma}[n_i, n_i](\mathbf{r}) \to -\frac{1}{r} \quad (r \to \infty),$$

(13)

whenever possible.

2.2. Choice of functionals for an open-shell system

In this subsection, we examine various exchange-correlation potentials for TDDFT calculations, namely the LDA-SIC, the Krieger–Li–Iafrate (KLI), and the Becke–Lee–Yang–Parr (BLYP) approximations (whose definitions are relegated to the appendix), and discuss which one is suitable for an open-shell system such as a Li atom.

Table 1 lists the orbital energy \(\varepsilon_{i\sigma}\) of each Kohn–Sham wavefunction in a ground-state Li atom (1s²2s) given by equation (1) using various exchange-correlation functionals: LDA (without SIC), LDA-SIC, KLI, and BLYP, all implemented using the GPS method, as well as the DFT result based on the optimized potential method (OPM) from [29] and the Hartree–Fock (HF) reference values from NIST [30]. For comparisons, experimentally determined binding energies of 1s and 2s electrons in a Li atom are 2.37 a.u. (atomic units) and 0.198 a.u., respectively [31]. In the self-interaction-free theory, the ground-state energy of the highest occupied orbital must equal the negative of the first ionization potential of an atom [32]. Also shown in table 1 is the total energy of each configuration, given by equation (7) or equation (11).

In table 1, we find that 1s₁ and 1s₈ electrons have a large energy difference of about 0.4 a.u. when they are calculated using OPM, whereas the HF calculation predicts little energy difference between them. The OPM is considered as the definition of the exact-exchange-only DFT [33]. The KLI approximation is developed as an improvement to the exchange-only Slater functional [34] by including the self-consistent correction term \(\Delta \omega_{ec}\) defined by equation (A.17) in the appendix. The KLI \((\Delta \omega_{ec} = 0)\) functional is an approximation to the exact-exchange OPM, which explains why their results in table 1 are very similar. Generally speaking, the self-consistent correction term is helpful in improving the total energy of an atom; see table A1 in the appendix. However, this term is responsible for the large difference between the 1s₁ and 1s₈ orbital energies. In our previous works with noble-gas atoms [35], TDDFT calculations were carried out using the LDA-SIC functional with a self-consistent correction term \(\Delta \omega_{ec}\) similar to \(\Delta \omega_{ec}\), which is defined by equation (A.6) in the appendix. It employs the same algorithm as KLI which can be generalized for time-dependent calculations to avoid iterative minimization in each time-step, as described in [36]. It is therefore inevitable that the LDA-SIC \((\Delta \omega_{ec} = 0)\) results follow the same trend as KLI and OPM with the large difference between the orbital energies of 1s₁ and 1s₈ electrons in table 1. This effect is undesirable in our PMD calculations since we intend to use the determinant of the Kohn–Sham orbitals as an approximation of the electron wave function; at least, such an approximation can be
and orbital is unoccupied and three-fold degenerate in the s-

In LDA-SIC calculations, the SIC orbital, therefore the HF entry for this orbital energy is left blank.

\[ r_{n} \]

calculated by using the local density approximation or the BLYP approximation, all implemented with the GPS method. Note that the local potential does not support a bound state in the unoccupied Δ.

The difference in shapes of a potential caused by the self-

potential, which corrects the asymptotic behaviour overall. The difference in shapes of a potential caused by the self-

potential in our calculation, but another no more than 0.01 a.u. The same trend exists between the KLI potential and the Slater potential to the LDA-SIC potential in our calculation, but doing so does not improve the orbital energies nor the total energy of an initial state, and therefore we opt not. Including such a BLYP correlation potential as shown in figure 2(d) in the limit of the adiabatic approximation is unlikely to help emulating the ionization-excitation channel in photoionization of a Li atom.

In table 2, we list the orbital energies and the total energies of an excited-state Li atom (1s^22p) and a Li^+ ion (1s^2) obtained using the LDA-SIC without a self-consistent correction term (Δw_{1s} = 0), which are used as an initial state of our TDDFT calculations. For comparisons, we also list HF calculations in [37] and [38]. We will refer to these values when discussing the Li-atom PMDs in section 3.

2.3. PMD calculations of a Li atom

For our calculations in this paper, we use the adiabatic approximation

\[ i \frac{\partial}{\partial t} \psi_{i}^{KS}(r, t) = \{ H_{0} + v_{i}^{KS}[n_{i}, n_{j}](r) \} \psi_{i}^{KS}(r, t) \]

Then, the initial state of each electron is evolved according to the time-dependent Kohn–Sham equations in the length gauge [24, 35]

\[ -i \frac{\partial}{\partial t} \psi_{i}^{KS}[n_{i}, n_{j}](r) + E(t) r \cos \theta \} \psi_{i}^{KS}(r, t) \]

### Table 1. Orbital energy \( \epsilon_{i}^{KS} \) of each electron in atomic units (1 a.u. = 27.2 eV) for the ground-state configuration (1s^22s) of a Li atom, calculated by using the local density approximation (LDA), the local density approximation with a self-interaction correction (LDA-SIC) with or without the self-consistent correction term (Δw_{1s}), the KLI approximation with or without the self-consistent correction term (Δw_{1s}), or the BLYP approximation, all implemented with the GPS method. Note that the 2p_{1} orbital is unoccupied and three-fold degenerate in the ground-state configuration. Also shown is the total energy of each state given by equation (7) or equation (11). In addition, we list the results based on the optimized potential method (OPM) in [29] and the HF reference calculations from NIST [30], for comparisons. The HF non-local potential does not support a bound state in the unoccupied 2p_{1} orbital, therefore the HF entry for this orbital energy is left blank.

<table>
<thead>
<tr>
<th>Method</th>
<th>LDA</th>
<th>LDA-SIC</th>
<th>KLI</th>
<th>BLYP</th>
<th>OPM[29]</th>
<th>HF[30]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Δw_{1s} = 0</td>
<td>Δw_{1s} = 0</td>
<td>Δv_{1s} = 0</td>
<td>Δv_{1s} = 0</td>
<td>Δv_{1s} = 0</td>
<td>Δv_{1s} = 0</td>
</tr>
<tr>
<td>Orbital energy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1s_{1}</td>
<td>-1.813 5</td>
<td>-1.993 0</td>
<td>-2.413 0</td>
<td>-2.081 6</td>
<td>-2.434 7</td>
<td>-1.851 3</td>
</tr>
<tr>
<td>1s_{2}</td>
<td>-1.804 6</td>
<td>-2.475 9</td>
<td>-2.421 8</td>
<td>-2.467 1</td>
<td>-2.420 8</td>
<td>-1.840 1</td>
</tr>
<tr>
<td>2s_{1}</td>
<td>-0.100 4</td>
<td>-0.195 7</td>
<td>-0.218 4</td>
<td>-0.196 4</td>
<td>-0.213 1</td>
<td>-0.078 0</td>
</tr>
<tr>
<td>2p_{1}</td>
<td>-0.035 9</td>
<td>-0.128 3</td>
<td>-0.152 7</td>
<td>-0.128 7</td>
<td>-0.145 4</td>
<td>-0.012 0</td>
</tr>
<tr>
<td>Total energy</td>
<td>-7.193 4</td>
<td>-7.434 2</td>
<td>-7.428 7</td>
<td>-7.432 4</td>
<td>-7.426 9</td>
<td>-7.483 6</td>
</tr>
</tbody>
</table>

reasonable if the absolute values of the Kohn–Sham orbital energies are close to the experimental ionization energies. In DFT, this is generally the case for the highest occupied orbitals (2s_{1} and 1s_{2} for the Li atom) but not for the other orbitals. To avoid large orbital energy differences between the electrons with opposite spins in the same shell, the self-

consistent correction term can be set to zero for open-shell systems. As table 1 shows, removing the self-consistent correction term \( \Delta w_{1s} \) in LDA-SIC changes the total energy of a Li atom by less than 0.01 a.u. (which is within the experimental errors in Zhu et al) but keeps the difference between the orbital energies of the 1s_{1} and 1s_{2} electrons quite small, in good accord with the accurate energy difference of 0.07 a.u. between the singlet and triplet states of a core-ionized Li^+ ion (1s2s) [30]. The LDA (without SIC) or the BLYP approximation does not produce a large gap between the 1s orbital energies either, but their agreement with the experimental energies is relatively poor. The KLI functional is numerically demanding for TDDFT because the calculation of the Slater potential involves complex-valued integrals once a wavefunction starts evolving in time. Therefore, we adapt the LDA-SIC functional with \( \Delta v_{1s} = 0 \) for our Li-atom TDDFT in this paper.

In figure 2, we plot exchange-correlation potentials \( v_{i}^{KS}[n_{i}, n_{j}](r) \) (scaled by \( r \) to remove singularity at the origin) of a ground-state Li atom according to LDA-SIC, KLI and BLYP approximations, whose corresponding energies are listed in table 1. Since a Li atom is an open-shell system, these potentials tend to be different for spin-up and spin-down electrons, except for the correlation part of the BLYP potential in figure 2(d). The small hump appears around the radius \( r = 1.5 \) a.u. for spin-up potentials in all cases, and it is due to the interaction of 1s_{1} and 2s_{1} electrons. Since there is only one spin-down electron in a Li atom, there is no such hump in spin-down potentials. The exchange-only LDA potential and the BLYP exchange-correlation potentials, shown in figures 2(a) and (d), respectively, do not have a proper asymptotic behaviour as equation (13) but rather vanish to zero as \( r \rightarrow \infty \). In LDA-SIC calculations, the SIC term shown in figure 2(b) is added to the exchange-only LDA potential, which corrects the asymptotic behaviour overall. The difference in shapes of a potential caused by the self-

consistent correction term \( \Delta w_{1s} \) in figure 2(b) is rather significant for spin-up electrons, even though the LDA-SIC total energy in table 1 with or without \( \Delta w_{1s} \) differ from one another no more than 0.01 a.u. The same trend exists between the KLI potential and the Slater potential (which is KLI with \( \Delta v_{1s} = 0 \)) in figure 2(c), that is, their shapes are rather different although their total energies in table 1 are fairly similar.

We could in principle add the correlation part of BLYP potential to the LDA-SIC potential in our calculation, but doing so does not improve the orbital energies nor the total energy of an initial state, and therefore we opt not. Including such a BLYP correlation potential as shown in figure 2(d) in the limit of the adiabatic approximation is unlikely to help emulating the ionization-excitation channel in photoionization of a Li atom.

In table 2, we list the orbital energies and the total energies of an excited-state Li atom (1s^22p) and a Li^+ ion (1s^2) obtained using the LDA-SIC without a self-consistent correction term (\( \Delta w_{1s} = 0 \)), which are used as an initial state of our TDDFT calculations. For comparisons, we also list HF calculations in [37] and [38]. We will refer to these values when discussing the Li-atom PMDs in section 3.
Table 2. Orbital energy $\varepsilon_i$ of each electron in atomic units, for the excited-state configuration (1s$^2$2p) of a Li atom and for a Li$^+$ ion (1$s^+$), calculated by using the LDA-SIC without the self-consistent correction term ($\Delta\varepsilon_{i\sigma}$ = 0). Note that the 2$s^o$ orbital is unoccupied for the excited-state configuration, whereas both 2$s^o$ and 2$p^o$ orbitals are unoccupied for the Li$^+$ ion. For comparisons, the HF calculations for Li$^+$ (1$s^2$2p) [37] and Li$^+$ [38] are also listed.

<table>
<thead>
<tr>
<th>Method</th>
<th>State</th>
<th>LDA-SIC (1s$^2$2p)</th>
<th>LDA-SIC (1$s^+$)</th>
<th>HF [37, 38] (1s$^2$2p)</th>
<th>HF [37, 38] (1$s^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial state</td>
<td></td>
<td>Li$^+$ (1s$^2$2p)</td>
<td>Li$^+$ (1$s^+$)</td>
<td>Li$^+$ (1s$^2$2p)</td>
<td>Li$^+$ (1$s^+$)</td>
</tr>
<tr>
<td>1$s^o$</td>
<td></td>
<td>-2.430 2</td>
<td>-2.792 4</td>
<td>-2.531 3</td>
<td>-2.792 3</td>
</tr>
<tr>
<td>1$s^+$</td>
<td></td>
<td>-2.442 7</td>
<td>-2.792 4</td>
<td>-2.530 0</td>
<td>-2.792 3</td>
</tr>
<tr>
<td>2$s^o$</td>
<td></td>
<td>-0.217 0</td>
<td>-0.572 5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2$p^o$</td>
<td></td>
<td>-0.149 0</td>
<td>-0.508 1</td>
<td>-0.128 7</td>
<td>—</td>
</tr>
<tr>
<td>Total energy</td>
<td></td>
<td>-7.358 6</td>
<td>-7.236 4</td>
<td>-7.365 1</td>
<td>-7.251 4</td>
</tr>
</tbody>
</table>

where $\mathcal{H}_0$ is the stationary-state Hamiltonian for the initial value problem given by equation (2), and

$$E(t) = \sqrt{I_0} \cos^2 \left( \frac{\omega_0 t}{2n} \right) \sin \omega_0 t,$$

with $I_0$ and $n$ being the peak intensity and the number of optical cycles ($T = 2\pi/\omega_0$) per pulse, respectively, of a driving laser of frequency $\omega_0$. In particular, we choose $\omega_0$ = 85 eV to be consistent with the experiment in [10], $I_0$ = 1 TW cm$^{-2}$, and $n$ = 500 which is roughly equivalent to 24 fs per pulse. In general, increasing $I_0$ makes a resulting PMD intensity higher, and decreasing $n$ makes the width of a PMD peak wider, but energy and angular dependence of a PMD are unchanged by either of these two parameters.

The time-dependent electron–electron interaction potential (14) is a functional of the time-dependent spin electron density

$$n_\sigma(r, t) = \sum_{i=1}^{N_\sigma} |\psi_{i\sigma}(r, t)|^2,$$

and calculated at each timestep using equation (4) from the solution $\psi_{i\sigma}(r, t)$ of equation (15).

In each timestep, the wavefunction $\psi_{i\sigma}(r, t)$ is split into inner and outer regions by a smooth masking function, and the PMD is found from the outer-region wavefunction that is propagated in the momentum space with the Volkov Hamiltonian in the velocity gauge [19, 35]. We study the PMD of each individual electron at the end of the time evolution $t = t_f$, given by

$$D_{i\sigma}(p, \theta_\sigma) = |\Phi_{i\sigma}^\dagger(p, t_f)|^2,$$
where $\tilde{\psi}^{\gamma}_{ss}(p, t_f)$ is the Fourier transform of the outer-region wavefunction, as well as the PMD of all electrons, given by

$$D(p, \theta_p) = \left| \sum_{\sigma} \sum_{i=1}^{N} \tilde{\psi}^{\gamma}_{ss}(p, t_f) \right|^2. \quad (19)$$

### 3. Results

Figure 3 is the main result of our paper and shows all-electron PMDs given by equation (19) for (a)–(c): the ground-state configuration $1s^22s$ and excited-state configurations $1s^22p$ of a Li atom, and for (d): a Li$^+$ ion ($1s^2$). They are to be compared with figure 2 in [10]. The valence orbital $2p$ of an excited-state Li atom is nonspherical, and therefore its ionization may depend on orbital orientations with respect to the laser polarization axis. In figure 3(b), the $2p$-orbital is in parallel with the driving-laser polarization (magnetic quantum number $m = 0$), and in figure 3(c) they are perpendicular to each other ($m = \pm 1$). In the experiment of [10], the magnetic sublevel populations of an excited Li-atom were mixed as $P (m = 0) = 0.68$ and $P(m = \pm 1) = 0.16$ when a pumping-laser polarization was in parallel with the XUV-laser polarization, and thus their PMD is equivalent to a weighted-average ($68:32$) between figures 3(b) and (c), which is shown in figures 3(e) and (f).

The PMDs of a Li atom in figures 3(a)–(c) contain two concentric peaks at the radii of $[p] = 2.4$ and $[p] = 1.2$ a.u., whereas the PMD of a Li$^+$ ion in figure 3(d) has one peak at $[p] = 0.8$ a.u. Fainter concentric circles of radii above $[p] = 2.7$ a.u. (corresponding to the photoelectron energy of $100 \text{ eV}$) are associated with two-photon ionizations of 1s electrons. On the other hand, photoelectron densities near the origin ($[p] < 0.5$ a.u.) in figures 3(a)–(c) are associated with double ionization (see figure 3 in [10]); for the excited-state PMD in figures 3(b) and (c), they are not spherical but dipole-like, in contrast to the ground-state PMD in figure 3(a), reflecting the orientation and symmetry of initial-state orbitals of the valence electron. Quantitative comparisons with the double-ionization PMDs of [10] are difficult since they did not distinguish different magnetic sublevels in their PMD measurements, but the close-up view of the weighted-averaged PMD in figure 3(f) has an oval-shape and shows a central peak near $p = 0$, consistent with figure 3(b) in Zhu et al. For the rest of the paper, we focus on studying the single-ionization PMDs between $[p] = 0.5$ a.u. and $[p] = 2.7$ a.u. induced by a single-photon absorption.

In [10], Zhu et al observed three distinctive photoelectron momenta at $[p] = 2.4$, 1.2 and 0.8 a.u. in single-ionization PMDs of both ground-state and excited-state Li atoms. Moreover, they found that the outermost peak at $[p] = 2.4$ a.u. diminishes its intensity whereas the innermost peak at $[p] = 0.8$ a.u. increases its intensity, when the initial state is prepared into the $1s^22p$ excited state. They argued that the PMD resulting from single-photon absorption of energy $\hbar \omega_0$ should have a peak at the radius $[39]$

$$[p] = \sqrt{2(\hbar \omega_0 - E_{\text{exc}} - I_p)}, \quad (20)$$

where $E_{\text{exc}}$ is an energy used to excite bound electrons (e.g., removal of an 1s electron to the continuum with simultaneous excitation of the valence electron $2s \rightarrow n\ell$) and $I_p$ is the binding energy of each electron. These three photoionization pathways in their account are schematically depicted in figure 4(a). The $2s \rightarrow n\ell$ excitations are called satellite transitions in general and believed to be caused by electron correlations [40, 41]. In particular, satellite transitions without changing an angular momentum ($\Delta \ell = 0$) are commonly referred as shake-up satellites [42]. According to the explanation given in [10], the two outer peaks in their Li-atom PMD are single-electron ionizations without a satellite transition ($E_{\text{exc}} = 0$), whereas the innermost peak is an inner-shell (1s) ionization with a satellite transition, i.e., an ionization-excitation channel. It is, however, somewhat unclear which specific satellite transitions are involved in the Li-atom...
PMDs of [10] and why they did not find more than one satellite transition. By comparison, photoelectron spectra of ground- and excited-state Li atoms measured using the synchrotron radiation source at BESSY in [43] and [44], respectively, exhibit multiple satellite-transition lines associated with 2s → 3s, 2p, 3p, 3d. To elucidate this point, we list the excitation energy $E_{\text{exc}}$ for the 2s → 3s and the 2s → 2p satellite transitions of a core-ionized Li$^+$ ion (1s2s $^3S$) in table 3. According to the R-matrix theory [45], they are the two most probable satellite transitions of a ground-state Li atom, accounting for 20% and 15% of all transitions, respectively, when driven by an 80-eV XUV pulse. Other satellite transitions are also possible but with less than 10% probabilities. As the driving-field energy increases to 100 eV, the 2s → 3s shake-up transition becomes more dominant (25%), but the 2s → 2p probability is still sizable (13%). If Zhu et al’s experiment [10] using an 85 eV pulse measured one transition in table 3, then the other transition should have been measured as well. The excitation energy implied by the separation between the two inner peaks of the Li-atom PMDs in [10] is about (1.25$^* 0.85$)/2 a.u. = 10.9 eV, which is fairly close to the experimentally measured $E_{\text{exc}} = 9.76$ eV for the 2s → 3s shake-up transition (1s2s $^3S$ → 1s3s $^3S$) in table 3. The R-matrix calculation in table 3 suggests, however, that the 2s → 2p satellite transition with $E_{\text{exc}} = 2.26$ eV (experimentally measured) is also probable for a core-ionized Li$^+$ ion. Driven by an XUV laser of energy $\hbar \omega_o = 85$ eV (3.1 a.u.), it would then produce another PMD peak at $|p| = \sqrt{2(3.1^*- 2.26/27.2 - 2.44)} = 1.1$ a.u. according to equation (20), with the HF calculation of the binding energy in table 1: $I_p = -\alpha_{2s} = 2.44$ a.u. The separation between this $2s \rightarrow 2p$ satellite line and the direct ionization line at $|p| = 1.2$ is only 0.1 a.u., which may have been too small to resolve with the momentum resolution in Zhu et al’s experiment ($\Delta p = 0.05$ a.u.). Another paper published later at FLASH in 2011 [17] achieved a better resolution of $\Delta p = 0.015$ a.u., and therefore it should be possible to distinguish them nowadays.

We could propose an alternative explanation to the three concentric peaks in Zhu et al’s measurement of a Li-atom PMD. In our TDDFT calculation of single-photon ionization of a multi-electron atom, each Kohn–Sham wavefunction may contribute a photoelectron whose momentum is given by

$$|p| = \sqrt{2\hbar \omega_o + \varepsilon_{\text{sat}}},$$

where $\varepsilon_{\text{sat}} (< 0)$ is the orbital energy of each electron in a Li atom. For example, the ground-state PMD in figure 3(a) exhibits two concentric peaks at the radii of $|p| = 2.4$ and 1.2 a.u., in agreement with the prediction given by equation (21) using $\hbar \omega_o = 85$ eV (3.1 a.u.) and orbital energies of the ground-state Li-atom from table 1, i.e., $\varepsilon_1 = -2.4$ and $\varepsilon_2 = -0.2$ a.u. As a comparison between tables 1 and 3 shows, the difference in orbital energies between the ground- and the excited-state configuration according to our LDA-SIC ($\Delta \omega_o = 0$ calculations is small (less than a few percent of an atomic unit), so that the concentric peaks of figures 3(b) and (c) also appear at $|p| = 2.4$ and 1.2 a.u., in accordance to Zhu et al’s result. The third, innermost peak at $|p| = 0.8$ a.u. in their measurement is not produced in our calculation with a Li atom but with a Li$^+$ ion (1s$^2$) in figure 3(d), and its location is consistent with the prediction by equation (21) using the orbital energy of a Li$^+$ ion ($\varepsilon_1 = -2.8$ a.u.) in table 2. This suggests that the innermost peak of the Li-atom PMD in Zhu et al’s measurement could have come from Li$^+$ ions, as shown in figure 4(b).

One possible source of Li$^+$ ion (1s$^2$) is the XUV ionization of a valence electron during the sequential double ionization. To see if such a process is plausible, we plot in figure 5 the ionization probabilities (evaluated as the integrated electron density outside the radius of 20 a.u.) of each Kohn–Sham wavefunction of a Li atom and a Li$^+$ ion during the calculation of figure 3. We find that the ionization probability of the valence (2s) electron of a Li atom is less than 0.002% at the XUV-laser intensity we use (I$o = 1$ TW cm$^{-2}$), which is too small to cause a non-adiabatic transition Li $\rightarrow$ Li$^+$ in the system. Calculations using higher intensity lasers may help to implement such a non-adiabatic scheme [46, 47], but they are computationally more demanding, and thus we do not attempt them in this paper.

Yet another possibility is that Li$^+$ ions are produced by the 670 nm optical pumping laser used for the preparation of an 2p-excitation state (1s$^2$2p). We did separate calculations with a ground-state Li atom using optical laser pulses to see how much valence-electron population is transferred to the continuum rather than promoted into the 2p orbital. Figure 6(a) shows the probabilities of ionization (solid line) and 2p-excitation (dotted line) of the Kohn–Sham orbital of a valence (2s) electron in a ground-state Li atom during the time evolution with a 20-cycle, 670 nm laser pulse of peak intensity $I_o = 1$ TW cm$^{-2}$. The corresponding Keldysh parameter for a ground-state Li atom (whose binding energy is
Figure 5. Ionization probability of Kohn–Sham wavefunctions during the time evolution with an XUV pulse of a photon energy $\omega_o = 85$ eV, linearly polarized along the $z$-axis with a peak intensity of $I_o = 1$ TW cm$^{-2}$, when the initial state of a Li atom is is chosen as (a) $1s^22s$ (ground state), (b) $1s^22p_0$ (magnetic quantum number $m = 0$), or (c) $1s^22p_{\pm1}$ ($m = \pm1$), respectively, whereas (d) is when the initial state is a Li$^+$ ion ($1s^2$). Note that the ionization probability of the valence electron in (a)–(c), shown with a dashed–dotted line, is scaled up ($\times10$) for clarity.

### Table 3. Excitation energies ($E_{\text{exc}}$) of a core-ionized Li$^+$ ion ($1s2s\ ^2S$) for the two most probable shake-up transitions. R-matrix calculations and experimental values (Expt.) are taken from [45]. In LDA-SIC calculations ($\Delta\omega_o = 0$), $E_{\text{exc}}$ is found as the difference between the initial-state ($1s2s\ ^2S$) total energy and the final-state ($1s3s\ ^2S$ or $1s2p\ ^2P$) total energy. Also shown is the probability (Prob.) of each transition in an 80 or 100 eV laser field according to the R-matrix theory.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>$E_{\text{exc}}$ (eV)</th>
<th>LDA-SIC</th>
<th>R-matrix</th>
<th>Expt.</th>
<th>80 eV</th>
<th>100 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s2s\ ^2S \rightarrow 1s3s\ ^2S$</td>
<td>9.60</td>
<td>9.70</td>
<td>9.76</td>
<td>19.92</td>
<td>24.83</td>
<td></td>
</tr>
<tr>
<td>$1s2s\ ^2S \rightarrow 1s2p\ ^2P$</td>
<td>2.09</td>
<td>2.22</td>
<td>2.26</td>
<td>14.77</td>
<td>12.55</td>
<td></td>
</tr>
</tbody>
</table>

$I_p = -\varepsilon_{2s} = 0.194$ 4 a.u. according to the HF reference in table 1) is $\gamma = 7.93$. With an optical driving laser pulse, ionization probability of inner orbital ($1s$) is negligibly small [17, 35] and therefore not shown. We find in figure 6(a) that the $2s \rightarrow 2p$ excitation probability undergoes Rabi oscillations, indicating a strong coupling induced by the resonant 670 nm laser field. Such Rabi oscillations are absent in figure 6(b) when the driving-laser frequency is detuned to 800 nm. The duration of FLASH pulses used in Zhu et al's experiment was 20 fs, and therefore it is likely that their measurement of an excited-state Li atom recorded the time-averaged electron populations oscillating between the ground- and excited-states. In fact, they estimated the fraction of excited states in their sample as $46 \pm 1\%$, which is reasonable if we assume Rabi oscillations. For a time-resolved measurement of an excited state, it would be necessary to reduce the duration of an XUV pulse to a few fs.

Zhu et al do not explicitly specify the peak intensity of the 670 nm optical laser. This intensity must be high enough to ensure efficient population transfer from the ground ($1s^22s$) state to the excited ($1s^22p$) state of the Li atom in the Rabi-flopping regime. We have found that this purpose is achieved
excited state are approximately the
for the excited state

10−20
-10
0
10
20
-20
0
20
time (fs)
time (fs)

Figure 6. Probability of the Li-atom valence (2s) electron for escaping to the continuum (solid line) and for the 2s → 2p excitation (dotted line) during the time evolution with a 20-cycle, linearly-polarized laser pulse of a peak intensity of $I_o = 1$ TW cm$^{-2}$ and a wavelength of (a) 670 nm (in resonance with the 2s–2p transition frequency) or (b) 800 nm. Also shown in the background are the laser fields $E(t)$ in arbitrary units.

at the peak intensity 1 TW cm$^{-2}$, as shown in figure 6(a). This is a relatively weak intensity if we consider non-resonant excitation or ionization of the ground state. Our calculation at a non-resonant wavelength 800 nm in figure 6(b) indeed shows small (<1%) ionization probability of the ground state. At the resonant wavelength 670 nm, however, our calculation predicts the ionization probability of more than 20% for the same peak intensity (figure 6(a)), indicating that the amount of Li$^+$ ions produced by the pumping 670 nm laser can be comparable with the amount of excited-state Li atoms. In fact, we find in figure 6(a) that the amounts of photoelectrons and electrons bound in the 2p excited state are approximately the same at the peak of the 670 nm laser pulse, supporting the possibility that an optical pumping laser produced Li$^+$ ions (1s$^2$) in Zhu et al’s measurement. This also explains why the intensity of the innermost peak in their excited-state PMD was stronger than in their ground-state measurement where the 670 nm field was absent. The ionization of a valence electron due to optical pumping lasers can be avoided by using shorter and less-intense 670 nm laser pulses, but then the 2s → 2p excitation will be less effective as well. In any case, these Li$^+$ ions produced by optical pumping lasers need to be removed in order for an accurate measurement of excited-state PMDs.

Figure 5 also shows that an XUV driving laser pulse is much more effective in ionizing the core electrons than the valence electron in TD-DFT, which is in fact consistent with the experiment by Zhu et al where the outermost spectrum has a much weaker intensity than the inner ones. To elaborate this point further, we plot in figure 7 the above-threshold ionization (ATI) spectra of individual electrons which are obtained by integrating individual PMDs given by equation (18) over polar angles $\theta$. Spectral peaks in figure 7 appear at $N/\hbar \omega_o + \varepsilon_{io}$, where $N$ is the number of absorbed XUV photons, and $\varepsilon_{io}$ is the eigenvalue of each bound electron given in table 1. The peaks of energy above 100 eV are associated with two-photon ionizations and appear exactly one photon energy ($\hbar \omega_o = 85$ eV) above the single-photon ionization peaks. Their intensities are several orders of magnitude lower than the single-ionization peaks, which may likely explain why [10] did not record them. Figures 7(a)–(c) show that the spectral yield from core orbitals (1s and 1s) is roughly 2–3 orders of magnitude larger than the valence orbital, consistent with the trend we find from the ionization probability in figure 5. Moreover, we find that the spectral yield of the valence electron is roughly ten times smaller when the initial state is in an excited state compared to when it is in the ground state, in agreement with Zhu et al’s experiment. Finally, it is interesting to note that the ATI spectra at low energy (<10 eV), which are associated with double-ionization, come solely from the valence orbital (2s for the ground-state, 2p for the excited state).

4. Conclusion

To summarize, we have investigated the photoelectron momentum distribution (PMD) of a state-prepared Li atom driven by an extreme ultraviolet (XUV) pulse of energy 85 eV, using time-dependent density functional theory (TD-DFT) in the limit of the adiabatic approximation. Two distinct photoelectron momenta appear in both the ground-state (1s$^2$2s) and the excited-state (1s$^2$2p) PMDs of a Li atom. Corresponding energies of the PMD peaks are found to be the sum of single photon energy from a driving laser and initial-state energies of core (1s) and valence (2s or 2p) orbitals predicted by DFT, whose values are in agreement with the FLASH measurement of singly-ionized Li-atom PMDs by Zhu et al [10]. The outermost peak associated with the valence electron weakens in intensity when a Li atom is initially in the excited state compared to when it is in the ground state, which is also in agreement with [10]. Our TD-DFT calculation of a Li atom does not predict the innermost peak measured in [10], but a separate calculation with a Li$^+$ ion indicates that it could be caused by electrons originating from Li$^+$ ions (1s$^2$). We find that the production of Li$^+$ ion is significantly enhanced in the presence the 670 nm...
optical pumping laser used for the excited-state preparation of Li atoms. We anticipate further developments in XUV photoionization experiments using free-electron lasers, which would help us develop TDDFT beyond the adiabatic approximation. Another promising technique to observe multi-electron PMDs is to use a combination of synchrotron radiation and narrow-bandwidth, tabletop laser systems to induce two-photon ionization, as was done very recently at SOLEIL facility [48]. In the future, we intend to study effects of driving-laser polarizations in PMDs of atoms to verify their findings.

Acknowledgments

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Appendix.

A.1. LDA-SIC functional

The LDA with a SIC for the exchange-correlation potential is given by [23]

$$v_{x,s}^{\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) \simeq v_{x,s}^{\text{LDA}}[n_{\sigma}](\mathbf{r}) - v_{\sigma}^{\text{SIC}}(\mathbf{r}),$$

(A.1)

where $v_{x,s}^{\text{LDA}}$ is the exchange-only LDA functional of spin electron density [27, 49]

$$v_{x,s}^{\text{LDA}}[n_{\sigma}](\mathbf{r}) = -\left(\frac{6}{\pi}n_{\sigma}(\mathbf{r})\right)^{1/3},$$

(A.2)
The corresponding exchange-correlation energy is

\[
E_{xc}[n_i, n_j] = E_x[n_i, n_j] - \sum_i \sum_j \left[ J[n_{ij}] + E_x[n_{ij}] \right].
\]  
(A.11)

where \( J \) is the Hartree-energy functional defined by equation (10), and

\[
E_x[n_i, n_j] = \frac{1}{2} E_x[2n_i] + \frac{1}{2} E_x[2n_j],
\]  
(A.12)

with

\[
E_x[n] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int n(r) r^{2/3} d^3r.
\]  
(A.13)

A.2. KLI functional

The KLI functional is another exchange-only approximation for the exchange-correlation potential, given by [50, 52]

\[
\Delta w_{\text{KLI}} \equiv (V^\text{KLI}_\sigma) - (V^\text{SI}_\sigma) = \sum_{j=1}^N (\mathcal{A}_{ij})^{-1}[(V^\text{SI}_{ij}) - (V^\text{SI}_{ji})].
\]  
(A.6)

where

\[
(V^\text{SI}_\sigma) = \int v^\text{SI}_\sigma(r) n_{ij}(r) d^3r,
\]  
(A.7)

\[
(V^\text{SI}_{ij}) = \int v^\text{SI}_{ij}(r) n_{ij}(r) d^3r,
\]  
(A.8)

\[
(V^\text{SI}_{ji}) = \int v^\text{SI}_{ji}(r) n_{ji}(r) d^3r,
\]  
(A.9)

and

\[
(A_{ij})^{-1} = \delta_{ij} - \int n_{ij}(r) n_{ij}(r) d^3r, \quad (A.10)
\]

where \( v^\text{KLI}_\sigma \) is defined as

\[
v^\text{KLI}_\sigma \simeq n_{ij}(r) \sim V^\text{KLI}_\sigma(r) = V^\text{SI}_\sigma(r) + \frac{1}{n_{\sigma}(r)} \sum_{i=1}^N n_{ij}(r) \Delta v_{ij},
\]  
(A.14)

where \( V^\text{SI}_\sigma \) is the self-interaction potential

\[
V^\text{SI}_\sigma = \frac{1}{n_{\sigma}(r)} \sum_{i=1}^N n_{ij}(r) v^\text{SI}_{ij}(r),
\]  
(A.15)
potential
\[ v_{\sigma}^{\text{HF}}(r) = \frac{-1}{\psi_0(r)} \sum_{j=1}^{N_\sigma} \int \frac{\psi_j(r') \psi_j^*(r') \psi_0(r)}{|r - r'|} d^3 r'. \] (A.16)

The self-consistent correction \( \Delta v_{\sigma} \) in equation (A.14) is found as
\[ \Delta v_{\sigma} = \langle v_{\sigma}^{\text{KLI}} \rangle - \langle v_{\sigma}^{\text{HF}} \rangle = \sum_{j=1}^{N_\sigma} (A_{ij} - 1) \{ \langle v_{ji}^S \rangle - \langle v_{ji}^S \rangle \}, \] (A.17)
where the \( N_\sigma \)-by-\( N_\sigma \) matrix \( A_{ij} \) is given by equation (A.10), and
\[ \langle v_{\sigma}^{\text{KLI}} \rangle = \int v_{\sigma}^{\text{KLI}}(r) n_{\sigma}(r) d^3 r, \] (A.18)
\[ \langle v_{\sigma}^{\text{HF}} \rangle = \int v_{\sigma}^{\text{HF}}(r) n_{\sigma}(r) d^3 r, \] (A.19)
\[ \langle v_{ji}^S(r) \rangle = \int v_{ji}^S(r) n_{ji}(r) d^3 r. \] (A.20)

The corresponding energy functional in the KLI approximation (A.14) is the Hartree–Fock exchange energy
\[ E_x[\psi_0] = -\frac{1}{2} \sum_{\sigma} \int d^3 r \int d^3 r' \frac{\psi_0^*(r') \psi_0^*(r') \psi_0^*(r) \psi_0^*(r)}{|r - r'|}. \] (A.21)

For calculations of an atom in particular, we may assume the Kohn–Sham wavefunction of the form
\[ \psi_\sigma(r) = \sum_{\ell,m} \frac{R_{\ell m}(r)}{r} Y_\ell^m(\theta, \phi), \] (A.22)
where \( Y_\ell^m(\theta, \phi) \) are spherical harmonics. Using the Laplace expansion
\[ \frac{1}{|r - r'|} = \sum_{\ell,m} \frac{4\pi(-1)^m}{2\ell + 1} \frac{r}{r_{\ell m}^{\ell+1}} Y_{\ell m}(\theta, \phi) Y_{\ell m}^*(\theta', \phi'), \] (A.23)
it follows that
\[ v_{\sigma}^{\text{HF}}(r) = -\frac{1}{R_{\ell m}^{\ell m}(r)} \sum_{j=1}^{N_\sigma} \sum_{\ell,m} \sum_{\ell'=-\ell}^{\ell} \left( \begin{array}{ccc} \ell & \ell' & \ell \\ 0 & 0 & 0 \end{array} \right)^2 W_{\ell m}^{\ell m}(r), \] (A.24)
where \( \left( \begin{array}{ccc} \ell & \ell & \ell \\ 0 & 0 & 0 \end{array} \right) \) are Wigner-3j coefficients, and
\[ W_{\ell m}^{\ell m}(r) \equiv \int \frac{r_\ell^{\ell'} R_{\ell m}^{(\ell)}(r') R_{\ell' m}^{(\ell)}(r') d^3 r'}. \] (A.25)

with \( r_\ell \equiv \min(r, r') \) and \( r_\ell \equiv \max(r, r') \). Note that \( \ell \) or \( \ell' \) is not a summation index but specific to each \( i \) or \( j \)th orbital, and hence it is enclosed in parentheses. In practice, \( W_{\ell m}^{\ell m}(r) \) is obtained by solving the following differential equation:
\[ -\frac{d^2}{d^2 r^2} + \frac{\ell(\ell + 1)}{r^2} Q_{\ell m}^{\ell m}(r) = (2\ell + 1) \frac{R_{\ell m}^{(\ell)}(r) R_{\ell' m}^{(\ell)}(r)}{r}, \] (A.26)
where \( Q_{\ell m}^{\ell m}(r) \equiv r W_{\ell m}^{\ell m}(r) \). The boundary conditions are
\[ Q_{\ell m}^{\ell m}(0) = 0, \] if \( \ell = 0 \)
\[ Q_{\ell m}^{\ell m}(\ell_{\max}) = \left\{ \begin{array}{ll} \frac{\delta_{\ell 0}}{1} \int_0^{\ell_{\max}} R_{\ell m}^{(\ell)}(r) R_{\ell' m}^{(\ell)}(r) r' d r & \text{otherwise.} \end{array} \right. \] (A.27)

### A.3. BLYP functional

The BLYP approximation uses the exchange energy functional of Becke [53] and the correlation energy functional of Lee, Yang, and Parr [54]. That is,
\[ E_{\text{xc}}^{\text{BLYP}} = \int \left( E_{\text{xc}}^{\text{DA}} - \beta \sum_{\sigma} \int n_{\sigma}^{4/3}(r) r^2 \right) + E_{\text{xc}}^{\text{LYP}}, \] (A.28)
where \( \beta = 0.0042, \) and
\[ x_\sigma(r) = \frac{|\nabla n_{\sigma}(r)|}{n_{\sigma}^{5/3}(r)}. \] (A.29)

The exchange and correlation energy functionals are, respectively,
\[ E_{\text{xc}}^{\text{DA}} = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \sum_{\sigma} \int n_{\sigma}^{4/3}(r) d^3 r, \] (A.30)
and [55]
\[ E_{\text{xc}}^{\text{LYP}} = -\frac{a \int \frac{4}{1 + d_{\text{nn}}^{-1/3}(r)} \left( \frac{n_{\sigma}(r) n_{\sigma}(r)}{n(r)} \right) d^3 r}{1 + d_{\text{nn}}^{-1/3}(r)}, \] (A.31)
\[ + \frac{47}{18} \int \frac{7}{18} |\nabla n_{\sigma}(r)|^2 - \frac{5}{2} \delta(r) \left( |\nabla n_{\sigma}(r)|^2 + |\nabla n_{\sigma}(r)|^2 \right), \] (A.31)
\[ + \frac{\delta(r) - 11}{9} \left( \frac{n_{\sigma}(r)}{n(r)} \right) |\nabla n_{\sigma}(r)|^2 - \frac{n_{\sigma}(r)}{n(r)} |\nabla n_{\sigma}(r)|^2 \right) \left( \frac{2}{3} n_{\sigma}(r) - n_{\sigma}^2(r) \right) \left( |\nabla n_{\sigma}(r)|^2 \right) \right)d^3 r, \] (A.31)
with \( a = 0.04918, b = 0.132, c = 0.2533, d = 0.349, \)
\[ C_{\text{F}} = \frac{3}{10} \left( 3\pi^2 \right)^{2/3}, \] and
\[ \delta(r) = c n_{\sigma}^{-1/3}(r) + \frac{d n_{\sigma}^{-1/3}(r)}{1 + d n_{\sigma}^{-1/3}(r)}. \] (A.32)
The corresponding BLYP functional for the exchange-correlation potential is [56]

\[ \psi_{\alpha}^{\text{BLYP}}[n_i, n_f](r) \simeq \psi_{\alpha}^{\text{VSDA}}[n_i](r) + \psi_{\alpha}^{\text{VP}}[n_i, n_f](r) \]

\[ = \frac{4}{3} \alpha r^{1/3}(r) \left\{ f(\gamma_r) - \frac{3}{8(6\pi^2)^{2/3}} f'(\gamma_r) \frac{\nabla^2 n_r(r)}{n_r^{2/3}(r)} + \frac{2}{2n^{2/3}(r)} \nabla n_r(r) \right\} \]

\[ - \frac{3}{4(6\pi^2)^{2/3}} \frac{f''(\gamma_r)}{n_r^{2/3}(r)} \left\{ \nabla^2 n_r(r) \frac{2}{3n_r^{2/3}(r)} \right\} \]  

where \( \gamma_r = \frac{\alpha}{4(6\pi^2)^{2/3}} \), and

\[ f(\gamma_r) = \frac{\gamma_r^2}{1 + 6/\gamma_r \sinh^{-1} \gamma_r} \].

The functional \( V^{\text{LDA}}_{\alpha} \) is given by equation (A.2), and

\[ V^{\text{LDA}}_{\alpha}[n_i, n_f](r) = -ar \left\{ \frac{\delta F}{\delta n_i}(r) + F[n_i](r) \right\} \]

\[ - \frac{2\alpha^{2/3} \delta G}{\delta n_i} \delta n_f \left\{ \frac{2G}{n_f^{2/3}(r)} + \frac{8}{3} \nabla^2 G[n_f](r) \right\} \]

\[ + \frac{ab}{4} \left\{ n_f(r) \nabla G[n_f](r) + 4\nabla G[n_f](r) + 4G[n_f](r) \nabla^2 n_f(r) \right\} \]

\[ + \frac{ab}{36} \left\{ 3n_f^{2/3} G[n_f](r) + 4\nabla n_f(r) \cdot \nabla G[n_f](r) + 4G[n_f](r) \nabla^2 n_f(r) \right\} \]

\[ + \frac{3ab}{36} \left\{ \nabla^2 n_f(r) + n_f(r) \nabla^2 n_f(r) \right\} \]  

(A.35)

The proper asymptotic condition (13) is not satisfied in the BLYP approximation, and we need to impose instead [57]

\[ \psi_{\alpha}^{\text{BLYP}}(r) \rightarrow - \frac{1}{\alpha} \frac{1}{r^2} \quad (r \rightarrow \infty), \]

(A.41)

where \( \alpha = 2\sqrt{-2}\mu \) with \( \mu \) being the chemical potential (negative of the single-ionization energy).

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