Time-dependent localized Hartree-Fock density-functional linear response approach for photoionization of atomic excited states

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We present a time-dependent localized Hartree-Fock density-functional linear response approach for the treatment of photoionization of atomic systems. This approach employs a spin-dependent localized Hartree-Fock exchange potential to calculate electron orbitals and kernel functions, and thus can be used to study the photoionization from atomic excited states. We have applied the approach to the calculation of photoionization cross sections of Ne ground state. The results are in agreement with available experimental data and have comparable accuracies with other ab initio theoretical results. We have also extended the approach to explore the photoionization from Ne excited states and obtained some results for the photoionization from outer-shell and inner-shell excited states.

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I. INTRODUCTION

Making use of local potentials and independent-particle response functions, density-functional theory (DFT) combined with linear response approximation (LRA) [1,2] has been successfully applied to study dynamic processes, such as photoabsorption [3–10] and dynamic polarizability [11–15], of atomic and molecular systems. The most attractive features of such an approach is its satisfactory accuracy and computational simplicity and efficiency. However, since the conventional DFT using traditional exchange-correlation (XC) potentials obtained from uniform electron gas, such as local-density approximation (LDA) [16,17] and generalized gradient approximation (GGA) [17–19], is a ground-state approach, the conventional DFT-LRA approach cannot only be used to investigate the dynamic processes associated with the ground state of a system. Even so, the counterpart of the DFT-LRA approach for the excited states has not yet been reported.

The difficulty encountered in the extension of the conventional DFT-LRA approach to the excited states stems from the XC potential used to characterize the excited states. A qualified XC potential for the excited states is required to be symmetry-dependent and self-interaction free and have a correct long-range behavior. The symmetry (such as electronic configuration, electron orbital angular momentum, and electron spin) of the XC potential is used to distinguish a state from the others, the self-interaction-free property of the XC potential is used to make the calculation of electron orbital energy accurate, and the correct asymmetric behavior of the XC potential is used to guarantee the Rydberg virtual orbitals which play a key role in autoionization resonances [7].

Recently, a localized Hartree-Fock (LHF) density-functional approach has been proposed and successfully applied to the ground-state calculation of atomic and molecular systems [20]. In this approach, the LHF exchange potential is self-interaction free and exhibits the correct long-range behavior. It only needs occupied orbitals and depends on the orbital symmetry of the state. More recently, a spin-dependent localized Hartree-Fock (SLHF) density-functional approach has been developed for the excited-state calculation of atomic and molecular systems [21]. This approach together with Slater’s diagonal sum rule [22] have been successfully used to calculate the energies of multiply excited states of valence electrons of atomic systems [21] and the energies of inner-shell excited states of closed-shell [23] and open-shell [24] atomic systems.

In this paper, we present a time-dependent localized Hartree-Fock density-functional linear response approach for the treatment of photoionization from atomic excited states by combining the SLHF DFT with LRA. In this approach, the SLHF exchange potential is employed to calculate both the Kohn-Sham (KS) electron orbitals and kernel functions. This is different from the approach used in Ref. [10] where the LHF potential was only used to calculate the electron orbitals. We have applied this approach to the calculation of photoionization cross sections (PICS) of Ne ground state and extended it to the computation of PICS of Ne excited states.

II. THEORETICAL METHODOLOGY

A. Linear response approximation of photoionization

Suppose that an atomic system is in a time-dependent external field along $z$ axis $E(t) = \tilde{E}_0 e^{-i \omega t}$ where $\tilde{E}_0$ is the amplitude and $\omega$ the frequency. In dipole approximation, the interaction potential of an electron and the external field is $\phi^{\mu}(r,t) = \phi^{\mu}(r,\omega)e^{-i \omega t}$, where $\phi^{\mu}(r,\omega) = z \tilde{E}_0$. Presence of the external field will induce a perturbation to the system and produce a redistribution of electron density [3]. In the case of weak field considered here, the dynamic response of the system has the same time dependence $e^{-i \omega t}$ as the field [8] and thus can be described by the LRA [25]. In frequency domain, total perturbing potential that an electron experiences can be expressed, in spin-dependent DFT framework [3,6–8], as

$$\phi_{a}^{\mu}(r,\omega) = \phi^{\mu}(r,\omega) + \sum_{\sigma} \int K_{\sigma a}(r,r') \delta_{\sigma \sigma'}(r',\omega) dr', \tag{1}$$

where, the second term on the right-hand side (RHS) is the field-induced potential, $\sigma$ is the electron spin ($\sigma = \uparrow$ for
Here, the first and second terms on the RHS represent the field-induced changes of Hartree potential and XC potential $V_{\text{xc}}(\mathbf{r})$, respectively.

The field-induced electron density $\delta \rho_{\sigma}(\mathbf{r}, \omega)$ is related to the total perturbing potential $\phi^{\text{SCF}}_{\sigma}$ by

$$K_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta V_{\text{xc}}(\mathbf{r})}{\delta \rho_{\sigma}(\mathbf{r})},$$

where $\chi_{\sigma}$ is the complex susceptibility given by

$$\chi_{\sigma}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i} \sum_{j} \frac{\gamma_{\sigma i}(\mathbf{r}, \mathbf{r}') \gamma_{\sigma j}(\mathbf{r}, \mathbf{r}')}{\omega - (\epsilon_{\sigma i} - \epsilon_{\sigma j}) + i\epsilon}.$$

Here, $\gamma_{\sigma i}(\mathbf{r}, \mathbf{r}') = \phi^{\text{xc}}_{\sigma i}(\mathbf{r}) \phi^{\text{xc}}_{\sigma i}(\mathbf{r}')$, $\phi^{\text{xc}}_{\sigma i}(\mathbf{r})$ is the $i$th electron spin-orbital, $\epsilon$ is a positive infinitesimal, and the notations $\sigma$ and $\sigma'$ represent that the sums run over all and occupied electron orbitals, respectively.

From Eqs. (1) and (3), $\phi^{\text{SCF}}_{\sigma}(\mathbf{r}, \omega)$ and $\delta \rho_{\sigma}(\mathbf{r}, \omega)$ have to be calculated in a self-consistent field procedure. Applying Eq. (1) to Eq. (3) and introducing a kernel function

$$N_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) = \chi_{\sigma}(\mathbf{r}, \mathbf{r}', \omega) K_{\sigma\sigma'}(\mathbf{r}', \mathbf{r}),$$

one obtains an equation for $\delta \rho_{\sigma}(\mathbf{r}, \omega)$

$$\sum_{\sigma'} \int \left[ \delta_{\sigma\sigma'} \delta_{\mathbf{r} - \mathbf{r}'} - N_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) \right] \delta \rho_{\sigma'}(\mathbf{r}', \omega) d\mathbf{r}' = \int \chi_{\sigma}(\mathbf{r}, \mathbf{r}', \omega) \phi^{\text{xc}}_{\sigma}(\mathbf{r}', \omega) d\mathbf{r}'.'

The polarizability $\alpha(\omega)$ is the ratio of the induced dipole moment to the external field strength

$$\alpha(\omega) = -\frac{1}{\epsilon_{0}} \sum_{\sigma} \int \frac{\delta \rho_{\sigma}(\mathbf{r}, \omega)}{c} d\mathbf{r} = -\frac{1}{\epsilon_{0}} \sum_{\sigma} \int \phi^{\text{xc}}_{\sigma}(\mathbf{r}, \omega) \chi_{\sigma}(\mathbf{r}, \mathbf{r}', \omega) \phi^{\text{SCF}}_{\sigma}(\mathbf{r}', \omega) d\mathbf{r}' d\mathbf{r}.'

The PICS $\sigma(\omega)$ is calculated by

$$\sigma(\omega) = \frac{4 \pi c}{c} \text{Im} \alpha(\omega),$$

where $c$ is the speed of light.

The LRA is usually referred to as a time-dependent method since it takes the time-dependent field-induced electron density into account. In contrast, if the field-induced electron density is neglected in Eq. (1), one has $\phi^{\text{SCF}}_{\sigma} = \phi^{\text{xc}}_{\sigma}$. In this case, the cross section Eq. (7) is reduced to the result of independent-particle approximation, which is referred to as a time-independent method.

### B. Electron spin-orbitals

To calculate the occupied electron spin-orbitals we use the SLHF density-functional approach [21,23,24]. In this approach, the electron spin-orbital $\phi_{\sigma i}(\mathbf{r})$ and orbital energy $\epsilon_{\sigma i}$ are calculated from the KS equation

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \phi_{\sigma i}(\mathbf{r}) = \epsilon_{\sigma i} \phi_{\sigma i}(\mathbf{r}),$$

where $V_{\text{eff}}$ is the local effective potential given by

$$V_{\text{eff}}(\mathbf{r}) = -\frac{Z}{r} + \sum_{\sigma} \int \frac{\rho_{\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}(\mathbf{r}).$$

In Eq. (10), the spin-dependent electron density is calculated by

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

where $N_{\sigma}$ is the number of electron with spin $\sigma$. On the RHS of Eq. (10), the first term is Coulomb potential, the second term is Hartree potential, and the third term $V_{\text{xc}}(\mathbf{r})$ is the XC potential. The XC potential can be decomposed into exchange potential $V_{\text{exchange}}(\mathbf{r})$ and correlation potential $V_{\text{correlation}}(\mathbf{r})$. The SLHF exchange potential $V_{\text{exchange,SLHF}}(\mathbf{r})$ is given by [21,23,24,26]

$$V_{\text{exchange,SLHF}}(\mathbf{r}) = -\sum_{\sigma} \frac{1}{\rho_{\sigma}(\mathbf{r})} \int \frac{\gamma_{\sigma i}(\mathbf{r}, \mathbf{r}') \gamma_{\sigma j}(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{1}{\rho_{\sigma}(\mathbf{r})} \int \gamma_{\sigma i}(\mathbf{r}, \mathbf{r}') \gamma_{\sigma j}(\mathbf{r}', \mathbf{r}) d\mathbf{r}'$$

The Green’s function

In Eq. (1) the sum over $j$ needs all the (occupied and unoccupied bound and continuum) electron orbitals. This makes it extremely difficult to accurately calculate $\chi_{\sigma}(\mathbf{r}, \mathbf{r}', \omega)$ directly from Eq. (4). To circumvent this difficulty, a Green’s function associated with the KS equation has been introduced to calculate $\chi_{\sigma}$ [3,6,8]. The Green’s function $G_{\sigma}(\mathbf{r}, \mathbf{r}', E)$ is calculated by
under appropriate boundary conditions. The Green’s function can be expanded in terms of a complete set of KS electron spin-orbitals as [3]

\[ G_\sigma(r, r', E) = \sum_j \frac{\gamma^j_\sigma(r, r')}{E - e_{i\sigma} \pm i\epsilon}. \] (13)

Applying Eq. (13) to Eq. (4) one has

\[ \chi_\sigma(r, r', \omega) = \sum_i \left[ \gamma^j_\sigma(r, r') G_\sigma(r, r', e_{i\sigma} + \hbar\omega) \right. \]

\[ + \left. \gamma^j_\sigma(r, r') G_\sigma^*(r, r', e_{i\sigma} - \hbar\omega) \right]. \] (14)

Thus with assistance of the Green’s function, only the occupied orbitals are needed to compute \( \chi_\sigma \).

III. COMPUTATIONAL DETAILS

A. Electron spin-orbitals

The electron spin-orbitals of an atomic system can be calculated by using the procedure previously developed in Refs. [21,24]. In spherical coordinates, the electron spin-orbital \( \varphi_{i\sigma}(r) \) is expressed as a product of a radial spin-orbital \( R_{n\ell m}(r) \) and a spherical harmonic \( Y_{\ell m}(\theta, \phi) \),

\[ \varphi_{i\sigma}(r) = \frac{R_{n\ell m}(r)}{r} Y_{\ell m}(\theta, \phi), \] (15)

where \( n \) is the principal quantum number, \( \ell \) is the orbital angular momentum quantum number, \( m \) is the azimuthal quantum number, and \( i \) is a set of quantum numbers except the spin \( \sigma \). The radial spin-orbital \( R_{n\ell m}(r) \) is calculated from the radial KS equation [21,24]

\[ \left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_{\sigma}^{\text{eff}}(r) \right] R_{n\ell m} = e_{n\ell m} R_{n\ell m}, \] (16)

where, \( v_{\sigma}^{\text{eff}}(r) \) is the radial effective potential [21]. To obtain high-precision electron spin-orbital and orbital energy, we use generalized pseudospectral (GPS) method [28] to discretize the radial KS Eq. (16). The GPS method associated with an appropriate mapping technique can overcome difficulties due to singularity at \( r=0 \) and long-tail at large \( r \) of the Coulomb interaction. It allows for nonuniform and optimal spatial discretization with the use of only a modest number of grid points. It has been shown that the GPS method is a very effective and efficient numerical algorithm for the high-precision solution of KS equation [21,24,29,30].

B. Green’s function

In spherical coordinates, the Green’s function can be expanded in terms of partial waves as

\[ G_\sigma(r, r', E) = \sum_{LM} Y^*_L(\theta, \phi) G_{L\sigma}(r, r', E) Y_L(\theta', \phi'), \] (17)

where, \( G_{L\sigma}(r, r', E) \) is the radial Green’s function, which, with the appropriate boundary conditions, is determined by an inhomogeneous equation [3,11]

\[ \left[ E + \frac{1}{2} \frac{d^2}{dr^2} + \frac{L(L+1)}{2r^2} + v_{\sigma}^{\text{eff}}(r) \right] G_{L\sigma}(r, r', E) = \frac{\delta(r - r')}{r^2}. \] (18)

Alternatively, the radial Green’s function can also be constructed from the solutions of a homogeneous equation

\[ \left[ -\frac{d^2}{dr^2} + \frac{L(L+1)}{2r^2} + 2v_{\sigma}^{\text{eff}}(r) - k^2 \right] u_{L\sigma}(r) = 0, \] (19)

where, \( k = \sqrt{2E} \). If \( \phi_{L\kappa\sigma}(r) \) is the solution of Eq. (19) being regular at the origin and \( \psi_{L\kappa\sigma}(r) \) the solution behaving asymptotically as \( r h^{(1)}_{\kappa}(kr) \) (where \( h^{(1)}_{\kappa} \) is the spherical Hankel function of the first kind), the radial Green’s function can be calculated by [11]

\[ G_{L\sigma}(r, r', E) = \frac{2 \phi_{L\kappa\sigma}(r \rightarrow r_a) \psi_{L\kappa\sigma}(r \rightarrow r_a)}{W}, \] (20)

where, \( r \rightarrow r_a \) refers to the smaller (larger) of \( r \) and \( r' \) and \( W = \phi_{L\kappa\sigma} \phi_{L\kappa\sigma}^{*} - \phi_{L\kappa\sigma}^{*} \phi_{L\kappa\sigma} \) is the Wronskian of \( \phi_{L\kappa\sigma} \) and \( \psi_{L\kappa\sigma} \).

C. Absorber

In principle, the boundary conditions at \( r \rightarrow \infty \) is required to calculate \( \psi_{L\kappa\sigma}(r) \). In reality, the boundary cannot be set at \( r \rightarrow \infty \). No matter how far the boundary is, as long as it is located at finite distance, the outgoing wave function \( \psi_{L\kappa\sigma}(r) \) with \( E>0 \) may reflect on the boundary, making the PICS oscillating artificially. To remove the reflection we introduce an absorber for each outgoing wave function. The absorber is characterized by an absorptive potential with a linear dependence of the radial coordinate

\[ U(r) = \begin{cases} 0, & 0 \leq r < r_a \\ -U_0 \frac{r - r_a}{r_{\max} - r_a}, & r_a \leq r \leq r_{\max} \\ \end{cases}, \] (21)

where \( r_{\max} \) is the radial coordinate of the boundary; \( U_0 \) and \( r_a \) are two parameters representing the strength and starting position of the absorber, respectively. Obviously, \( r_{\max} - r_a \) represents the width of the absorber. Similar absorbers have been used in the wave packet method of molecular collisions [31,32] and photoionization of molecules and atomic clusters recently [33].

When taking the absorptive potential into account the outgoing wave function is calculated from an equation obtained by replacing \( v_{\sigma}^{\text{eff}}(r) \) with \( v_{\sigma}^{\text{eff}}(r) + iU(r) \) in Eq. (19). Since the behavior of an outgoing wave function depends on electron spin-orbitals through both \( v_{\sigma}^{\text{eff}}(r) \) and \( k(E) \) the absorber parameters may be different for different electron spin-orbitals.
D. Susceptibility and cross sections

In spherical coordinates, the susceptibility $\chi_\alpha(r, r', \omega)$ can also be expanded in the partial waves [11]

$$\chi_\alpha(r, r', \omega) = \sum_{lm} Y_{lm}(\theta, \phi) \chi_{lm}(r, r', \omega) Y_{lm}(\theta', \phi').$$  \hspace{1cm} (22)

From Eqs. (14), (15), (17), and (22), the partial wave susceptibility $\chi_{lm}(r, r', \omega)$ is calculated by

$$\chi_{lm}(r, r', \omega) = \frac{1}{4\pi} \sum_{\alpha' \alpha} \sum_L w_{\alpha' \alpha} \frac{R_{\alpha' \alpha}(r) R_{\alpha' \alpha}(r')}{r} \langle (0l0|L0) \rangle^2$$

$$\times \left[ G_{L\alpha}(r, r', e_{\alpha' \alpha} + \hbar \omega) + G_{L\alpha}^*(r, r', e_{\alpha' \alpha} - \hbar \omega) \right].$$ \hspace{1cm} (23)

Furthermore, expanding $\delta \rho_\alpha(r, \omega)$ in the partial waves

$$\delta \rho_\alpha(r, \omega) = \sum_{\alpha'} N_{\alpha \alpha'}(r, r', \omega) \delta \rho_{\alpha'}(r, r'),$$

and from Eq. (6), we obtain

$$\delta \rho_{\alpha\beta}(r, \omega) = E_0 \sqrt{\frac{4\pi}{3}} \int \chi_{\alpha\beta}(r, \omega, r') r'^3 dr' \delta_{\alpha\beta} \delta_{\alpha\beta}$$

$$+ \sum_{\alpha'} \int N_{\alpha \alpha'}(r, r', \omega) \delta \rho_{\alpha'}(r, r') r'^2 dr',$$ \hspace{1cm} (24)

where $N_{\alpha \alpha'}(r, r', \omega)$ is the partial wave component in the partial wave expansion

$$N_{\alpha \alpha'}(r, r') = \sum_l Y_{lm}(\theta, \phi) Y_{lm}(\theta', \phi').$$

Solving Eq. (24) one obtains the partial wave component $\delta \rho_{\alpha\beta}(r, \omega)$. From Eq. (7), the polarizability $\alpha(\omega)$ is given by

$$\alpha(\omega) = -\frac{1}{E_0} \sqrt{\frac{4\pi}{3}} \sum_{\alpha} \int \delta \rho_{\alpha\beta}(r, \omega) r'^3 dr.$$ \hspace{1cm} (25)

The PICS $\sigma(\omega)$ is calculated from Eq. (8) by using $\alpha(\omega)$.

IV. RESULTS AND DISCUSSION

A. Photoionization from the ground state of Ne

To test the approach developed in the preceding sections, we first apply it to the calculation of PICS from the ground state of Ne. The total PICS is plotted in Fig. 1, where the solid and dashed lines are the results of time-dependent spin-dependent localized Hartree-Fock (TDSLHF) and time-independent spin-dependent localized Hartree-Fock (TISLHF) methods, respectively. Also plotted in this figure are recent experimental data [34,35] for comparison. It is shown that the TISLHF PICS are substantially larger than the experimental results in a broad range of lower photon energy. The maximum deviations to the experimental results in Ref. [34] and Ref. [35] are 35.9% and 31.3% before the resonance region and 33.0% and 24.6% after the resonance region, respectively. The TDSLHF cross sections, however, are much closer to the experimental results and show significant improvement in spite of the underestimate near the ionization threshold (IT) of 2p electron. Apart from the energy region adjacent to the IT of 2p electron where the maximum deviations are 31.0% and 32.4%, the discrepancies to the experimental results in Ref. [34] and Ref. [35] are not more than 20.0% and 20.0% before the resonance region and less than 19.9% and 6.1% after the resonance region, respectively. In the range of photon energy shown in Fig. 1, except a small stepwise enhancement due to the contribution of 2s electron photoionization at the IT energy of 21 eV, the TISLHF PICS are structureless and decrease monotonically above the IT of 2s electron. The TDSLHF PICS, however, appear a series of sharp resonances in the energy region from

![FIG. 2. (Color online) Autoionization resonances in the total photoionization cross sections near the ionization threshold of 2p electron: (a) The results of TDSLHF method and (b) the results of TISLHF method with the 2s electron orbital energy being replaced by the experimental value. The resonance peaks 1 to 8 are produced by the transitions 2s → np with n = 3 to 10, respectively. The open circles are the numerical results and the solid lines are the fitted results to the Fano profile.](image_url)
In the higher energy region, both TDSLHF and TISLHF results are getting closer and approach to the experimental results. The sharp resonances in the PICS are produced by the resonant transitions $2s \rightarrow np$ from the ground state $1s^22s^22p^6$ to autoionization states $1s^22s2p^6np$ with $n=3$ to 10. In Fig.

### TABLE I. Profile parameters of the autoionization resonances produced by the transitions from the ground state of Ne to the Rydberg series $1s^22s2p^6np$ with $n=3$ to 8.

| Resonant transition | Approach | $\sigma_0$ (Mb) | $\Gamma$ (meV) | $q$ | $q^2$ | $E_r$ (eV) |
|---------------------|----------|-----------------|----------------|----|-------|-------------|
| $2s \rightarrow 3p$ | TDSLHF$^a$ | 8.34            | 12.80          | −4.03 | 0.551 | 43.358      |
|                     | S-TDSLHF$^b$ | 8.40            | 15.23          | −3.40 | 0.619 | 45.447      |
|                     | S-EXX+ALDA$^c$ | 8.09            | 17.9           | −3.18 | 0.547 | 45.438      |
|                     | S-TDLSDA$^d$ | 8.28            | 18.04          | −2.40 | 0.764 | 45.453      |
|                     | TDLDA$^e$   | 8.18            | 13.90          | −3.69 | 0.514 | 46.253      |
|                     | $R$ matrix$^f$ | 34.9            |                |       |       | 45.534      |
|                     | Expt.$^g$   | 8.6 ± 0.6       | 13 ± 2         | −1.6 ± 0.2 | 0.70 ± 0.07 | 45.546 ± 0.008 |
| $2s \rightarrow 4p$ | TDSLHF$^a$ | 8.12            | 3.89           | −4.35 | 0.543 | 45.028      |
|                     | S-TDSLHF$^b$ | 8.15            | 4.55           | −3.74 | 0.606 | 47.115      |
|                     | S-EXX+ALDA$^c$ | 7.89            | 5.5            | −3.35 | 0.528 | 47.093      |
|                     | S-TDLSDA$^d$ | 8.06            | 5.14           | −2.62 | 0.783 | 47.098      |
|                     | TDLDA$^e$   | 7.98            | 3.86           | −3.95 | 0.505 | 47.397      |
|                     | $R$ matrix$^f$ | 6.65            |                |       |       | 47.111      |
|                     | Expt.$^g$   | 8.0 ± 0.6       | 4.5 ± 1.5      | −1.6 ± 0.3 | 0.70 ± 0.07 | 47.121 ± 0.005 |
| $2s \rightarrow 5p$ | TDSLHF$^a$ | 8.05            | 1.55           | −4.47 | 0.537 | 45.625      |
|                     | S-TDSLHF$^b$ | 8.06            | 1.81           | −3.85 | 0.600 | 47.713      |
|                     | S-TDLSDA$^d$ | 7.91            | 2.20           | −2.72 | 0.783 | 47.683      |
|                     | TDLDA$^e$   | 7.91            | 1.62           | −4.05 | 0.502 | 47.814      |
|                     | $R$ matrix$^f$ | 2.47            |                |       |       | 47.692      |
|                     | Expt.$^g$   | 8.2 ± 0.6       | 2 ± 1          | −1.6 ± 0.5 | 0.70 ± 0.14 | 47.692 ± 0.005 |
| $2s \rightarrow 6p$ | TDSLHF$^a$ | 8.00            | 0.89           | −4.57 | 0.539 | 45.901      |
|                     | S-TDSLHF$^b$ | 8.00            | 1.04           | −3.94 | 0.601 | 47.989      |
|                     | $R$ matrix$^f$ | 1.28            |                |       |       | 47.967      |
|                     | Expt.$^g$   | 8.0 ± 0.6       | 4.5 ± 1.5      | −1.6 ± 0.3 | 0.70 ± 0.07 | 47.967 ± 0.006 |
| $2s \rightarrow 7p$ | TDSLHF$^a$ | 7.99            | 0.43           | −4.99 | 0.555 | 46.075      |
|                     | S-TDSLHF$^b$ | 8.01            | 0.59           | −3.88 | 0.585 | 48.163      |
|                     | $R$ matrix$^f$ | 0.73            |                |       |       | 48.119      |
|                     | Expt.$^g$   | 8.0 ± 0.6       | 4.5 ± 1.5      | −1.6 ± 0.3 | 0.70 ± 0.07 | 48.116 ± 0.006 |
| $2s \rightarrow 8p$ | TDSLHF$^a$ | 7.94            | 0.37           | −4.54 | 0.534 | 46.171      |
|                     | S-TDSLHF$^b$ | 7.96            | 0.42           | −3.92 | 0.605 | 48.258      |
|                     | $R$ matrix$^f$ | 0.46            |                |       |       | 48.211      |
|                     | Expt.$^g$   | 8.0 ± 0.6       | 4.5 ± 1.5      | −1.6 ± 0.3 | 0.70 ± 0.07 | 48.207 ± 0.006 |

$^a$TDSLHF results.
$^b$TDSLHF results with the experimental $2s$ electron orbital energy.
$^c$EXX+ALDA results with the experimental $2s$ electron orbital energy.
$^d$TDLSDA results with the experimental $2s$ electron orbital energy.
$^e$TDLDA results.
$^f$R-matrix results.
$^g$Experimental results.

43.0 to 46.4 eV. In the higher energy region, both TDSLHF and TISLHF results are getting closer and approach to the experimental results.
we show the details of the resonances in open circles. To quantitatively analyze the resonances and estimate the autoionization widths we fit the resonances to the Fano profile

\[
\sigma(\omega) = \sigma_0 \left[ \eta^2 \frac{(q + \kappa)^2}{1 + \kappa^2} - \eta^2 + 1 \right],
\]

where \(\kappa = 2(\omega - E_r)/\Gamma\), \(E_r\) is the resonance position, \(q\) is the profile index, \(\Gamma\) is the linewidth of the resonance profile, \(\eta^2\) is the correlation coefficient, and \(\sigma_0\) is the cross section without correlation. In Fig. 2(a) we show the fitted resonances in the solid line. The fitted resonance profile parameters are given in Table I in the rows with TDSLHF and shown in Fig. 3 with open squares. Also listed in Table I and shown in Fig. 3 are the available experimental results \[37\] and the theoretical results of the time-dependent density-functional method employing exact exchange-only KS potential and adiabatic-local-density-approximation exchange-correlation kernel with shifted 2s orbital energy \(\text{S-EXX+ALDA} \[10\]), time-dependent local spin-density approximation with shifted 2s orbital energy \(\text{S-TDLSDA} \[6\]), time-dependent local-density approximation \(\text{TDLDA} \[7\]), and \text{R-matrix} method \(\text{R-matrix} \[38\]), for comparison. Figure 3(a) shows that for the cross section \(\sigma_0\) the TDSLHF results are in good agreement with the experimental values and overall a little bit better than the other theoretical results. The deviations to the results of S-EXX+ALDA, S-TDLSDA, TDLDA, and ex-

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**FIG. 3.** (Color online) Profile parameters of autoionization resonances: (a) cross section \(\sigma_0\), (b) linewidth \(\Gamma\), (c) profile index \(q\), (d) correlation coefficient \(\eta^2\), and (e) resonance position \(E_r\).
experiments are less than 3.1%, 1.8%, 2.0%, and 3.0%, respectively. For the linewidth $\Gamma$ shown in Fig. 3(b) the TDSLHF results are close to the TDLDA results and better than those of S-EXX+ALDA, S-TDLSDA, and $R$ matrix compared to the experimental results. The maximum deviations of the results of TDSLHF, S-EXX+ALDA, S-TDLSDA, TDLDA, and $R$ matrix to the experimental results are 22.5%, 37.7%, 38.7%, 19.0%, and 168.5%, respectively. For the line profile index $q$ in Fig. 3(c), all the theoretical results are much smaller than the experimental results and the TDSLHF results are close to those of TDLDA. The maximum discrepancies of the results of TDSLHF, S-EXX+ALDA, S-TDLSDA, and TDLDA to the experimental results are 179.4%, 109.4%, 70.0%, and 153.1%, respectively. For the correlation coefficient $\eta^2$ shown in Fig. 3(d), the TDSLHF results are very close to those of S-EXX+ALDA and TDLDA but smaller than the S-TDLSDA results and experimental data. The maximum discrepancies of the TDSLHF results to those of S-EXX+ALDA, S-TDLSDA, TDLDA, and experiments are 2.8%, 31.4%, 7.5%, and 22.4%, respectively. As for the resonance position $E_r$ in Fig. 3(e), all the resonances in TDSLHF PICS are about 2 eV shift to the lower photon energy with respect to the experimental data. Similar phenomena were also found in Refs. [6,10]. This discrepancy mainly stems from the deviation of the 2s electron orbital energy from the experimental value [6]. Furthermore, we notice that the 2s electron orbital energy from the TDSLHF calculation is $-1.707$ a.u. which is about 2.04 eV higher than the experimental value $-1.782$ a.u. [39]. To explore influence of the orbital energy to the PICS and resonance profiles we have also performed a TDSLHF calculation with the 2s electron orbital energy being replaced by the experimental value in the calculation of the Green’s function. The calculated and fitted PICS in the resonance energy region are shown in Fig. 2(b) in the open circles and solid line, respectively. The fitted resonance profile parameters are listed in Table I in the rows with S-TDSLHF and shown in Fig. 3 with open circles. It is shown that with the 2s electron orbital energy replaced by the experimental value the resonances shift to the higher photon energy about 2 eV and the calculated resonance positions $E_r$ are in very good agreement with the experimental results. When using the theoretical value of the 2s electron orbital energy, the maximum discrepancies of the TDSLHF results to those of S-EXX+ALDA, S-TDLSDA, TDLDA, $R$ matrix, and experiments are 4.6%, 4.6%, 6.3%, 4.8%, and 4.8%, respectively. While when using the experimental value of the 2s electron orbital energy, the maximum deviations of the S-TDSLHF results to
those of S-EXX+ALDA, S-TDLSDA, TDLDA, \( R \) matrix, and experiments are reduced to 0.05%, 0.06%, 1.74%, 0.19%, and 0.22%, respectively. In addition, all the other resonance profile parameters, particularly \( \Gamma \) and \( \eta^2 \), are also significantly improved and closer to the experimental values. The maximum deviations of the S-TDSLHF results to the experimental results are reduced to 2.3%, 17.2%, 140.6%, and 13.4%, respectively, for \( \sigma_0 \), \( \Gamma \), \( q \), and \( \eta^2 \).

### B. Photoionization from outer-shell excited states of Ne

For the photoionization from Ne excited states, particularly for those with autoionization resonances, both experi-

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**TABLE II.** Autoionization resonance peak positions (in eV) for the photoionizations from Ne outer-shell excited states \( \{1s, 2s, 2p, 3s, 3p\}nl \), with \( n=3-4 \) and \( l=0-2 \).

| Initial states | \{3s\} | \{3p\} | \{3d\} | \{4s\} | \{4p\} | \{4d\} |
|----------------|--------|--------|--------|--------|--------|--------|
| \( 2p \rightarrow 3s \) | 23.829 | 26.150 | 23.527 | 24.863 | 26.509 |
| \( 4s \) | 24.526 | 26.738 | 29.139 | 27.693 | 29.554 |
| \( 5s \) | 25.383 | 27.630 | 30.153 | 26.839 | 30.452 |
| \( 6s \) | 25.759 | 28.014 | 30.575 | 27.206 | 30.896 |
| \( 7s \) | 26.013 | 28.221 | 30.803 | 27.405 | 31.119 |
| \( 8s \) | 28.406 | 30.928 | 30.549 | 29.293 | 31.250 |
| \( 9s \) | 31.043 | 29.386 | 31.334 |
| \( 10s \) | 31.416 |
| \( 3d \) | 24.855 | 27.078 | 29.565 | 26.371 | 30.001 |
| \( 4d \) | 25.516 | 27.769 | 30.850 | 27.453 | 30.670 |
| \( 5d \) | 25.826 | 28.085 | 30.850 | 27.453 | 31.173 |
| \( 6d \) | 26.066 | 28.264 | 30.850 | 27.453 | 31.282 |
| \( 7d \) | 30.961 | 31.358 |
| \( 2p \rightarrow 3s \) | 29.984 | 30.382 | 30.656 | 30.594 | 30.638 |
| \( 4s \) | 35.446 | 36.948 | 38.389 | 38.302 | 38.559 |
| \( 5s \) | 36.809 | 38.447 | 40.406 | 40.722 | 41.081 |
| \( 6s \) | 36.036 | 37.378 | 38.327 | 38.213 | 38.412 |
| \( 4d \) | 37.018 | 38.580 | 40.479 | 40.697 | 41.021 |
| \( 5d \) | 42.194 | 42.635 |
| \( 2s \rightarrow 2p \) | 22.994 | 23.032 | 23.032 | 23.048 | 23.081 | 23.056 |
| \( 3p \) | 46.964 | 49.187 | 51.685 | 48.719 | 52.129 |
| \( 4p \) | 48.510 | 50.798 | 53.310 | 50.044 | 53.682 |
| \( 5p \) | 49.075 | 51.381 | 53.960 | 50.572 | 54.265 |
| \( 6p \) | 49.359 | 51.659 | 54.260 | 50.833 | 54.577 |
| \( 7p \) | 49.623 | 51.835 | 54.420 | 50.986 | 54.745 |
| \( 8p \) | 52.036 | 54.332 | 51.136 | 52.883 | 54.845 |
| \( 9p \) | 54.654 | 54.923 |
| \( 10p \) | 53.098 | 55.013 |
| \( 11p \) | 55.114 |
| \( 2s \rightarrow 3p \) | 56.790 | 57.457 | 57.892 | 57.786 | 57.979 | 57.911 |
| \( 4p \) | 59.650 | 61.242 | 62.926 | 62.818 | 62.940 | 63.218 |
| \( 5p \) | 60.817 | 62.458 | 64.412 | 64.404 | 64.747 | 65.147 |

\( \{1s, 2s, 2p, 3s, 3p\}nl \) is the abbreviation of the core electron configuration.
Time-dependent localized Hartree-Fock lines are the results of TDSLHF and TISLHF methods, respectively. Experimental data [40,41] and theoretical results [41–45] are scarce. One of the advantages of the proposed approach is that it can be used to calculate the photoionization from excited states of atomic systems. Such kind of calculation can provide insight into interchannel interference and orbital relaxation in the photoionization processes from the excited states. We first apply the proposed approach to the computation of PICS of Ne outer-shell excited states. In Fig. 4, we show, in the solid and dashed lines, the total PICS of TDSLHF method and TISLHF method for the photoionization from the outer-shell excited state 1s₁s₁2s₂2p₃2p₅3s₁ of Ne, respectively. In Fig. 5 we show the details of autoionization resonances in the total PICS. It is shown that the total PICS can be divided into five regions A–E. They are separated by the steps at ITs in the TISLHF PICS. The first region A starts from the IT of 3s₁ electron and ends at the IT of 2p₁ electron followed by two series of sharp autoionization resonances in the TDSLHF PICS. These two series of resonances are produced by the transitions of a 2p₁ electron to the higher bound s₁ and d₁ orbitals, respectively, and thus converge to the IT of 2p₁ electron, as shown in Fig. 5(a). Unlike the PICS of the ground state which increase with photon energy near the IT of 2p electron, the PICS of the excited state decrease with photon energy near the IT of the 3s₁ electron. The second region B starts from the IT of 2p₁ electron and ends at the IT of 2p₁ electron. In this region there are also two series of sharp resonances in the PICS, as shown in Fig. 5(b). They are induced by the transitions of a 2p₁ electron to the higher bound s₁ and d₁ orbitals, respectively, and converge to the IT of 2p₁ electron. The third region C starts from the IT of 2p₁ electron and ends at the IT of 2s₁ electron followed by a series of sharp resonances produced by the transitions of a 2s₁ electron to the higher bound p₁ orbitals, as shown in Fig. 5(c). Note that one resonance produced by the transition 2s₁ → 2p₁ in this series is located in the lower energy region A in Fig. 5(a). The fourth region D starts from the IT of 2s₁ electron and ends at the IT of 2s₁ electron. This region consists of a series of sharp resonances produced by the transitions of a 2s₁ electron to the higher bound p₁ orbitals as shown in Fig. 5(d). The last region E covers the energy region from the IT of 2s₁ electron to the maximum energy shown in Fig. 4. In this region the PICS are structureless since the next autoionization resonances occur at very high energy region when a 1s₁ electron is resonantly pumped to the higher bound p₁ orbitals. We have also performed the calculation of PICS from other outer-shell excited states of Ne. The total PICS have the similar structures as those from the excited state 1s₁s₁2s₂2p₂p₃₂p₅3s₁ shown in Fig. 4.

Interchannel interference has a significant impact on the autoionization resonances in the photoionization from excited states. Due to the interference of autoionization channels, the profiles of autoionization resonances, particularly...
those produced by the transitions from the same electron orbital such as those shown in Figs. 5(a) and 5(b), are no longer the standard Fano profile. Thus it is impossible to accurately evaluate autoionization resonance profile parameters by fitting the resonances to Fano profile. However, we can still estimate the peak position for each autoionization resonance very well. In Table II, we list the peak positions of autoionization resonances for the photoionizations from Ne inner-shell excited states. The PICS can be divided into four regions. Our calculation shows that for an autoionization resonance produced by the transition from an inner-shell electron orbital to an autoionization electron orbital, the deeper of the inner-shell electron orbital and the lower of the autoionization electron orbital, the larger of the relaxation effect.

### C. Photoionization from inner-shell excited states of Ne

As another application we extend the proposed approach to the calculation of PICS of Ne inner-shell excited states. In Fig. 6 we plot the total PICS of TDSLHF and TISLHF methods in the solid and dashed lines, respectively, for the photoionization from Ne inner-shell excited state \(1s_{1} 1s_{2} 2s_{1} 2s_{2} 2p_{1}^{2} 2p_{2} \uparrow n_{l} \) with \( n = 3 \rightarrow 4 \) and \( l = 0 \rightarrow 2 \).

![Image](https://via.placeholder.com/150)

**TABLE III. Autoionization resonance peak positions (in eV) for the photoionizations from Ne inner-shell excited states \( \{1s_{1} 1s_{2} 2s_{1} 2s_{2} 2p_{1}^{2} 2p_{2} \uparrow n_{l} \} \) with \( n = 3 \rightarrow 4 \) and \( l = 0 \rightarrow 2 \).**

| Resonant transition | \( \{2s_{1} 2s_{2} \} \) | \( \{3p_{1} \} \) | \( \{3d_{1} \} \) | \( \{4s_{1} \} \) | \( \{4p_{1} \} \) | \( \{4d_{1} \} \) |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| \( 2p_{1} \rightarrow 3s_{1} \) | 21.655 | 23.821 | 21.478 | 22.681 | 24.128 |
| \( 4s_{1} \) | 22.188 | 24.648 | 26.738 | 25.356 | 27.086 |
| \( 5s_{1} \) | 23.026 | 25.595 | 27.742 | 24.626 | 26.245 | 27.973 |
| \( 6s_{1} \) | 23.394 | 25.998 | 28.167 | 24.994 | 26.656 | 28.403 |
| \( 7s_{1} \) | 23.644 | 26.215 | 28.381 | 25.187 | 26.866 | 28.629 |
| \( 8s_{1} \) | 26.411 | 28.509 | 25.328 | 26.988 | 28.756 |
| \( 9s_{1} \) | 28.624 | 25.499 | 27.094 | 28.841 |
| \( 10s_{1} \) | 28.768 | 27.224 | 28.947 |
| \( 3d_{1} \) | 22.488 | 24.923 | 27.141 | 24.163 | 25.739 | 27.508 |
| \( 4d_{1} \) | 23.143 | 25.720 | 27.908 | 24.784 | 26.398 | 28.150 |
| \( 5d_{1} \) | 23.453 | 26.060 | 28.248 | 25.073 | 26.707 | 28.493 |
| \( 6d_{1} \) | 23.686 | 26.254 | 28.427 | 25.233 | 26.907 | 28.678 |
| \( 7d_{1} \) | 26.444 | 28.542 | 25.369 | 27.015 | 28.790 |
| \( 8d_{1} \) | 28.654 | 25.543 | 27.118 | 28.866 |
| \( 9d_{1} \) | 28.801 | 27.249 | 29.048 |
| \( 2p_{1} \rightarrow 3s_{1} \) | 30.711 | 30.942 | 31.198 | 31.122 | 31.135 | 31.201 |
| \( 4s_{1} \) | 36.393 | 37.647 | 39.089 | 38.904 | 39.002 | 39.263 |
| \( 5s_{1} \) | 37.780 | 39.152 | 41.141 | 41.176 | 41.440 | 41.821 |
| \( 6s_{1} \) | 42.937 | 43.440 |
| \( 3d_{1} \) | 36.994 | 38.088 | 39.037 | 38.842 | 38.918 | 39.108 |
| \( 4d_{1} \) | 37.987 | 39.288 | 41.206 | 41.127 | 41.421 | 41.750 |
| \( 5d_{1} \) | 42.412 | 42.390 | 42.725 | 43.190 |
| \( 2p_{1} \rightarrow 3p_{1} \) | 45.735 | 49.307 | 52.955 | 52.955 | 53.921 | 54.304 |
| \( 4p_{1} \) | 62.154 | 64.049 | 65.944 | 65.944 | 67.060 |
| \( 5p_{1} \) | 63.375 | 65.337 | 67.391 | 67.391 | 69.507 | 70.107 |

\( \{1s_{1} 1s_{2} 2s_{1} 2s_{2} 2p_{1}^{2} 2p_{2} \uparrow n_{l} \} \) is the abbreviation of the core electron configuration.
gions A–D. Each region starts from the IT of an electron orbital and ends at the IT of next lower-energy electron orbital. It is shown that the TISLHF PICS are structureless apart from a stepwise enhancement at each IT. The TDSLHF PICS, however, contain several series sharp autoionization resonances, as shown in Fig. 7.

The region A starts from the IT of 3s\textsubscript{1} electron and ends at the IT of 2p\textsubscript{1} electron followed by two series of autoionization resonances, as shown in Fig. 7(a). The two series resonances are produced by the transitions of a 2p\textsubscript{1} electron to the higher bound s\textsubscript{1} and d\textsubscript{1} orbitals and converge to the IT of 2p\textsubscript{1} electron. The cross sections near the IT of 3s\textsubscript{1} electron again decrease with photon energy. The region B starts from the IT of 2p\textsubscript{1} electron and ends at the IT of 2p\textsubscript{1} electron. In this region there are also two series of autoionization resonances. They are produced by the transitions of a 2p\textsubscript{1} electron to the higher bound s\textsubscript{1} and d\textsubscript{1} orbitals and converge to the IT of 2p\textsubscript{1} electron, as shown in Fig. 7(b). The region C begins with the IT of 2p\textsubscript{1} electron and ends at the IT of 2s\textsubscript{1} electron. In this region, there is a series of autoionization resonances induced by the transitions of the 2s\textsubscript{1} electron to the higher bound p\textsubscript{1} orbitals, as shown in Fig. 7(c). The last region D starts from the IT of 2s\textsubscript{1} electron and ends at the maximum energy shown in Fig. 6. In this region, the PICS are structureless since the autoionization resonances will occur at very high energy.

We have also estimated the peak positions for the autoionization resonances. In Table III, we list the peak positions of autoionization resonances for the photoionization from Ne inner-shell excited states 1s\textsubscript{1}1s\textsubscript{2}2s\textsubscript{1}2s\textsubscript{2}2p\textsubscript{1}p\textsubscript{1}nl\textsubscript{1} for $n=3–4$ and $l=0–2$. Our calculation shows again that for an autoionization resonance due to the transition from an inner-shell electron orbital to an autoionization electron orbital, the deeper of the inner-shell electron orbital and the lower of the autoionization electron orbital, the larger of the relaxation effect.

V. CONCLUSION

In this paper, we propose a time-dependent localized Hartree-Fock density-functional linear response approach for the treatment of photoionization of atomic systems. In this approach, the occupied electron orbitals are calculated by solving the KS equation with SLHF exchange potential, the complex susceptibility is calculated by using the occupied electron orbitals and corresponding Green’s functions, and the PICS are calculated by using the susceptibility. The relaxation of electron orbitals is taken into account through the Green’s functions. To remove the possible reflection of the wave function on the boundary an absorber is imposed for each outgoing wave function in the calculation. The absorber is characterized by an absorptive potential with a linear dependence of coordinates. Since the SLHF exchange potential has a correct long-range behavior and can be used to accurately calculate the electron orbitals of atomic excited states, the proposed approach is suitable for the calculation of photoionization from excited states of atomic systems. We have applied this approach to the calculation of PICS of Ne ground state. The results are in agreement with available experimental and have comparable accuracies with other ab initio theoretical results. We have also extended this approach to the computation of PICS of Ne excited states. The total PICS can be divided into several regions. Each region starts from the IT of an electron orbital and ends at the IT of the next lower-energy electron orbital. In each region there is one or two series of autoionization resonances produced by the resonant transitions of an electron from inner-shell electron orbitals to autoionization electron orbitals with higher energies. For the autoionization resonances produced by the transitions from inner-shell electron orbitals to autoionization electron orbitals, the deeper of the inner-shell electron orbitals and the lower of the autoionization electron orbitals, the larger of the orbital relaxation effect.

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