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Sturmian approach to single photoionization of many electron atoms and molecules

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Abstract. The application of generalized Sturmian functions to the study of single photoionization of different atomic and molecular systems is illustrated using model potentials. Sturmian functions have been used successfully to study single and double ionization by electron impact on He, while their implementation to molecular systems is still under development. The radial part of the scattering function is expanded in a generalized Sturmian basis. The solution of the resulting matrix problem provides the expansion coefficients. The latter yield directly the photoionization transition amplitude and thus the cross sections. Here we show our preliminary results for He and Ne atoms on one hand, and for CH\textsubscript{4} and H\textsubscript{2}O molecules on the other.

1. Introduction

In the past, many different theoretical methods have been developed to study photoionization of atoms and molecules. However, the accurate representation of the continuum states of atomic systems, and more so for molecular systems, still represents a big challenge. In more recent years, the Sturmian approach, using Generalized Sturmian Functions (GSFs), has been applied successfully for the study of several atomic ionization processes [1–4], and the extension of the method to molecular systems is under development.

In the present contribution, we report the preliminary results of the use of the Sturmian approach to study the single photoionization of simple molecules, specially for CH\textsubscript{4} and H\textsubscript{2}O. To do so, we first validate our approach by studying many–electron atoms; here we show the cases of He and Ne.

As the description of the electronic structure of molecules is, in general, a difficult task, many different approximations have been developed, such as the one center expansion (OCE) [5, 6], where all the coordinates of electrons are referred to a common center, located in the center of mass of the system. We shall use this approximation, which is known to give reasonable good results for special cases where a central nucleus exists, as for CH\textsubscript{4} and H\textsubscript{2}O [5–8].

Atomic units (\(\hbar = e = m_e = 1\)) are used throughout unless otherwise indicated.
2. Theory

2.1. Photoionization

In order to study single photoionization of atoms and molecules, we start with the non–relativistic time–dependent Schrödinger equation (TDSE), to which a Fourier transform is applied. We use the first order perturbation theory over the wave function of the continuum (final) states, and the dipolar approximation, either length or velocity gauges, to describe the interaction of the radiation field with the system under study. We solve the resulting driven equation, i.e., the time–independent Schrödinger equation (TISE) for the continuum final state wave function \( \Phi^{(1)} \)

\[
\left[ \omega_k + \frac{1}{2} \nabla^2 - U (r) \right] \Phi^{(1)} (r, \omega) = \mathcal{F} (\omega) \hat{D}^{(s)} \Phi^{(0)} (r),
\]

where \( \omega \) is the energy of the incident photon, \( \omega_k = \omega - \omega_0 \) is the energy of the resulting photoelectron, \( \mathcal{F} (\omega) \) is the Fourier transform of the radiation field, \( U (r) \) is the scattering potential felt by the photoelectron, \( \Phi^{(0)} (r) \) is the initial state wave function of energy \( \omega_0 \), and \( \hat{D}^{(s)} \) is the dipolar operator in length (L) or velocity (V) gauges. For the radiation field we consider a laser pulse with a sine squared envelope.

Before solving equation (1), we separate the continuum wave function in its radial and angular parts

\[
\Phi^{(1)} (r, \omega) = \sum_{\ell m} \varphi^{(1)}_{\ell E} (r, \omega) Y^m_{\ell} (\Omega)
\]

and the radial part is expanded in a basis set

\[
\varphi^{(1)}_{\ell E} (r, \omega) = \frac{1}{r} \sum_n a^{(\ell, E)}_n (\omega) S^{(\ell, E)}_n (r).
\]

In this work, for the radial function \( S^{(\ell, E)}_n (r) \), we choose to use GSFs. Their implementation to study ionization processes in molecular systems has not been done before.

2.2. Generalized Sturmian functions

In general, Sturmian functions are the set of solutions to a Sturm–Liouville problem. In particular, GSFs are solutions (regular at the origin, i.e., \( S^{(\ell, E)}_n (r = 0) = 0 \), of the radial equation

\[
\left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell (\ell + 1)}{2r^2} + \mathcal{U} (r) - E \right) S^{(\ell, E)}_n (r) = -\beta^{(\ell, E)}_n \mathcal{V} (r) S^{(\ell, E)}_n (r)
\]

where \( E \) is an externally fixed parameter, the energy of the continuum state which one wants to describe; \( \mathcal{U} (r) \) is called the auxiliary potential, usually of long–range, dictating, together with \( E \), the asymptotic behavior of \( S^{(\ell, E)}_n (r) \); \( \mathcal{V} (r) \) is a short–range generating potential; and \( \beta^{(\ell, E)}_n \) are the eigenvalues of the problem. Further details on GSFs are given in the review [1].

In this work we use a Yukawa potential with an energy–dependent parameter as generating potential, and a Coulomb potential with charge \(-1\) as auxiliary potential, in order to attribute to the radial functions the correct asymptotic form. The use of GSFs as a basis set allows us to perform very efficient calculations because of their intrinsic physical properties: each function has the exact asymptotic behavior dictated by the auxiliary potential for the given energy \( E \) [1]. When photoionizing neutral targets, the continuum final states describing the photoelectron is, asymptotically, a Coulomb wave with charge \(-1\).
2.3. Description of atomic systems

To study single photoionization of atomic systems, we start with the single-active approximation (SAE) [9], where the ionized electron is in a screened potential. For He we use the Herman–Skillman model potential [10]

\[ U_{HS}(r) = \frac{Z_1}{r} + \left( \frac{Z_2}{r} + \frac{Z_3}{r} \right) e^{-\alpha r}, \]  

(5)

with the parameters \( Z_1 = Z_3 = -1, \) \( Z_2 = -2 \) and \( \alpha = 3.5499. \) For Ne we use the model potential given by Rogers et al [11]

\[ U_{Par}(r) = -\frac{1}{r} \left[ Z - \nu + \sum_{n=1}^{n_{\text{max}}} N_n e^{-\alpha_n r} \right], \]  

(6)

where \( \nu \) is the number of electrons in the parental ion, \( N_n \) is the number of electrons in the \( n \)-th shell, \( n_{\text{max}} \) is the maximum value for \( n \) in the parental ion, and \( \alpha_n \) is a screening parameter.

In figure 1 we plot the effective charges, \( rU(r) \), associated with the model potentials (5) and (6) for He and Ne. One sees how the nuclear charge is screened by electrons remaining in the parental ion. The asymptotic charge is always \(-1\), as it should be, indicating that these potentials can be used to study single photoionization.

![Figure 1](image)

**Figure 1.** (Color online) Effective charges, \( rU(r) \), for H, He and Ne. For H (black – – –) we use the Coulomb potential; for He (red — —) the Herman–Skillman potential (5), and for Ne (blue — —) the parametric model potential by Rogers et al (6).

The diagonalization of the potential (5) (respectively (6)) provides the ground state description of He (respectively Ne): (i) the eigenfunction of the valence electron to be used in the TISE (1); (ii) the first ionization energy, reported in table 1.

2.4. Description of molecular systems

In this contribution we use two different model potentials to describe molecular systems. When ionization experiments are performed the real orientation of the molecule is generally undetermined, so that an average over those orientations must be considered. This issue is dealt with an angular average over the molecular potentials before we calculate any continuum
Table 1. Ground state energies $\omega_0$ of valence electrons. For He we use the Herman–Skillman potential (5) and for Ne the parametric potential (6). Each energy is compared with experimental first ionization energies $I$.

| Atom | level | $\omega_0$ (a.u.) | $I$ (a.u.) |
|------|-------|-------------------|------------|
| He   | 1s    | -0.903717         | 0.903569   |
| Ne   | 2p    | -0.795327         | 0.792482   |

Table 2. Ground state energies $\omega_0$ of valence electrons obtained using the model potential (10), for the studied MOs of CH$_4$ and H$_2$O. The energies are compared with the values reported by Moccia [5, 6].

| Molecule | MO level | $\alpha$ | $\omega_0$ (a.u.) | $\omega_0$ (a.u.) |
|----------|----------|----------|-------------------|-------------------|
| CH$_4$   | 1t$_2$   | 2p       | -1.381368         | -0.504199         |
| H$_2$O   | 1b$_1$   | 3p       | -0.571085         | -0.495400         |
3. Results

To study single photoionization in atoms and molecules, we solve the TISE (1), using the potentials (5) or (6) for atomic systems and either (10) or (7) for molecular systems. After expanding the scattering radial wave function (3) in GSFs, the resulting equation is projected over all the elements of the basis set to obtain a linear system of equations for the expansion coefficients. We solve the associated matrix system, and the obtained coefficients can be used to extract the photoionization cross sections, taking advantage of the GSFs basis asymptotic properties [1]. For all the targets considered in this contribution, we used 60 basis functions.

We show below the results for atoms and molecules separately, and shall compare them with a selection of experimental data and other theoretical calculations (two at maximum). This is enough to show the cross sections general features and the kind of agreement one may find. Although we do not expect the SAE to be sufficiently accurate at low energies, we shall show the cross sections versus photoelectron energy starting from the threshold where theories have most difficulties in reproducing the measurements.

3.1. Atoms

For both He and Ne we calculated the photoionization cross sections from the valence orbital in both length and velocity gauges. For He the results are shown in figure 3. They are compared with an *ab initio* nonresonant cross section by Granados–Castro and Sanz–Vicario [18], and with the experimental data of Samson *et al* [19]; the agreement between our results and other theoretical and experimental data is good, in particular in the length gauge.

![Figure 3](image-url) (Color online) Photoionization cross section in Mb vs. photoelectron energy for He. We compare our results calculated in the length (green – – –) and velocity (red ——) gauges with a nonresonant cross section [18] (blue ·····) and with experimental data [19] (black ●).

![Figure 4](image-url) (Color online) Same as figure 3 for Ne. Our results are compared with theoretical results [20] (blue ·····) and [21] (orange — —), and with experimental data [22] (black ▲).

In figure 4 we plot the results for Ne and compare them with the theoretical calculations of McGuire [20] and of Farnoux and Lamoureux [21], and with the experimental data of Samson *et al* [22]. Again our calculations in length gauge show a good agreement. However, a large magnitude difference with the velocity gauge is found. To crosscheck our results, we reproduced them with an equivalent calculation performed using B-splines [23]. We may also exclude any inconsistency or shortcoming of the Sturmian method that could be associated to the \( \ell \neq 0 \) nature of the initial state orbitals; indeed, the same approach reproduces exactly, within
numerical precision, the photoionization cross sections from np orbitals for H. The discrepancy in cross sections obtained with both gauges is known, and has been observed in other calculations for Ne [24] and, for example, in similar approaches for Ar and Xe [25, 26]; it may be explained by a high sensitivity to the quality of the ground state wave function (in particular at short distances from the nucleus), as well the exclusion of different many–body effects as the intrachannel interactions and virtual double excitations in the ground state [26]. It is clearly necessary to use more sophisticated model potentials in order to obtain a better agreement between both gauges. However, the original purpose of this work is to study photoionization in molecules, the atomic case serving to test the methodology and to indicate the range of validity of the SAE.

3.2. Molecules

We now turn to the photoionization from the outer valence MOs of CH$_4$ and H$_2$O. The results in length and velocity gauges for the MO 1$t_2$ of CH$_4$ are shown in figure 5. They are compared with the theoretical calculations by Kilcoyne et al [27], obtained using the ground state inversion potential method/diffraction, which calculates the total ionization amplitude with a superposition of the atomic ionization amplitudes. The cross section is also compared with the theoretical results by Stener et al [8], based on a time–dependent DFT method, and with the experimental data of Backx and van der Wiel [28]. We see that our results obtained using the central potential (10) show an excellent agreement in the asymptotic energy region. For small energies, however, the experimental cross section is largely underestimated. The result of the calculation using the non–central potential (7) in velocity gauge are in a better agreement with the experimental data in all the considered energy range. At small photoelectron energies, the cross section peak is comparable to that obtained by the two other calculations.

![Figure 5](image1.png)

**Figure 5.** (Color online) Photoionization cross section in Mb vs. photoelectron energy from the MO 1$t_2$ of CH$_4$. We compare our results in length (green – – –) and velocity (red ——) gauges using the central potential (10) and using the non–central potential (7) (blue — —), with the theoretical calculations [27] (maroon · · · ·) and [8] (orange — —), and with experimental data [28] (black ■).

Our results for the MO 1$b_1$ of H$_2$O are shown in figure 6. They are compared with the results of Kilcoyne et al [27] and Stener et al [8], and with the experimental data of Banna et al [29].

![Figure 6](image2.png)

**Figure 6.** (Color online) Photoionization cross section in Mb vs. photoelectron energy from the MO 1$b_1$ of H$_2$O. We compare our results in length (green – – –) and velocity (red ——) gauges using the central potential (10) and using the non–central potential (7) (blue — —), with the theoretical calculations [27] (maroon · · · ·) and [8] (orange — —), and with experimental data [29] (black ♦).
Similar to the results of CH$_4$, the use of (10) yields a very good agreement in the asymptotic energy region, and this time the region for small energies is slightly better represented. It is worth noting how the three theoretical approaches yield cross sections which differ substantially in the range 0 to 1 a.u. As for CH$_4$, our results with potential (7) are in reasonable agreement with the experimental data for all the calculated energies.

Similarly to the observation made for atoms, photoionization cross sections for molecular systems are also very sensitive to the selected potential and to the quality of the ground state wave function. This is clearly put in evidence by the different shapes observed in figures 5 or 6. More sophisticated descriptions of both potentials and ground states wave functions will deliver better results, but overall the cross sections presented in these figures have good general features.

4. Summary and perspectives
Considering we are using one–electron wave functions, the GSF method yields good results for the photoionization of atoms, in particular in the length gauge. With a built-in correct asymptotic behavior, the GSF are particularly efficient: using only a relatively small number of basis elements, the method produces converged results (scattering wave functions and transition amplitudes). Turning to applications in molecular systems, the same GSF method combined with the OCE and model molecular potentials, central and non–central, is used to describe the molecular continuum states. Again, using a relatively small number of basis elements, we obtained reasonable results, specially for high photoelectron energies. However, the description of the continuum for lower energies is still incomplete, and a more accurate treatment of the valence MOs and the scattering potentials themselves must be done in order to improve the results. Also full consideration of the spatial orientation of the molecule must be included in our calculations. Work in this direction is on the way.

The next step will be to study single ionization by electron collisions with molecules, using in particular the non–central potential (7). Issues related to the spatial orientation of the molecule are of great importance.

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