A Sturmian approach to photoionization of molecules

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Abstract

An accurate theoretical description of photoionization processes is necessary in order to understand a great variety of physical and chemical phenomena, and allows one to test correlation effects of the target. Compared to the case of many-electron atoms several extra challenges occur for molecules. The scattering problem is generally multicenter and highly non-central. Additionally, the molecular orientation with respect to the polarization of the radiation field has to be taken into account. These features make the computational task much more cumbersome and expensive than for atomic targets. In order to calculate cross sections one needs to describe the ejected electron with a continuum wavefunction with appropriate Coulomb asymptotic conditions. Making a number of initial approximations, many different theoretical/numerical methods have been proposed over the years. However, depending on the complexity of the molecule, agreement among them is not uniform, and many features of the experimental data are not so well reproduced. This is illustrated through a number of examples. In order to have a global theoretical overview we present a survey of most of the methods available in the literature, indicating their application to different molecules. Within a Born–Oppenheimer, one-center expansion and single active electron approximation, we then introduce a Sturmian approach to describe photoionization of molecular targets. The method is based on the use of generalized Sturmian functions for which correct boundary conditions can be chosen. This property makes the method computationally efficient, as illustrated with results for H_2O, NH_3 and CH_4.

keywords: Photoionization molecules; Theoretical methods; Generalized Sturmian functions; Cross sections

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Contents

1   Introduction

The quantum description of both bound and unbound orbitals are necessary ingredients to study collisions with atoms and molecules. The study of single photoionization (PI) provides an indirect tool to test our capacity to describe correctly the target before and after the interaction, and thus correlation and many-body effects. PI plays an important role beyond atomic and molecular physics, since it has a wide variety of applications, such as astrophysics[1–3], planetary[4–6], atmospheric[7,8], plasma[9–11] or medical physics[12,13]. Also PI helps to understand different processes in surfaces, as structural changes upon surface adsorption, quantifying the relationship between shape resonances and the bond lengths[14–17]; or to characterize the relation between gas, chemisorbed and solid-state phases in surface reactions[18–21].

In the last few years, a Sturmian approach[22,23] has been introduced to study single and double ionization of atoms induced by electron or photon impact[24]. It is the purpose of this contribution to extend, implement and apply such an approach to the PI of molecular targets. The Hamiltonian for molecules being generally multicenter and highly non-central makes life harder than in the case of atomic targets. Indeed, the absence of any spherical symmetry couples different angular momenta from different atomic orbitals (AOs) that conform the molecular orbitals (MOs), and thus convergence of "traditional" methods is considerably more difficult to achieve. Additionally, there are various many-body effects that can be important in ionization processes, such as the relaxation of all MOs, due to the creation of a hole (ionized electron), or the change of the remaining pair correlation energies because of such relaxation. An issue which does not arise in PI of atoms is the orientation of the molecular target. In most experiments the molecule is randomly oriented and this must be taken into account within the theoretical calculations.

When leaving an atomic or molecular target, an ionized electron needs to be described accurately by a continuum wavefunction, which has a well defined boundary conditions. Over the years, quite a few methods have been proposed and applied successfully to atoms. The extension of these methods and their computational codes to molecular targets is not straightforward, as several complications arise beyond the many-body nature of the problem, and not all of them can provide the correct asymptotic form. Different approaches have been applied to a large variety of molecules ranging from the smallest one, H_2, up to, e.g., DNA basis. The success of each method depends on the considered molecule and photon energy range, the validity of some approximations, and possibly on convergence issues or limitations related to the numerical implementation.

Except for small molecules, experimental data are not so abundant, and do not always span the whole photoelectron energy range; they therefore do not permit to fully assess the quality of different theoretical descriptions. As several theories are often not in agreement with each other and with experimental data, especially close to threshold, we made a survey of the different methods applied to PI in molecules. For each, we briefly indicate the main ingredients, the advantages and possible limitations. We also found useful to draw a list (rather complete to the best of our knowledge) of all molecules for which PI has been investigated theoretically.

In order to calculate the transition amplitudes for single PI in atomic or molecular systems, many considerations must be taken into account. Usually the starting point is the treatment of the ionized electron as a one-electron function, the one-center expansion (OCE). In many cases, the vibrational structure of the molecule can be ignored, especially in high energy collisions, so that one may work within the Born–Oppenheimer (BO) approximation. Also, in order to simplify the calculations, the frozen core (FC) approximation and the static exchange approximation (SEA) are considered. It is within this frame, together with a model molecular potential, that we implement the generalized Sturmian approach. In the literature several Sturmian functions implementations exist, as reviewed, e.g., in the introductions of References 22 and 23. Similarly to previous publications on scattering studies (see the recent review 22 and references therein), in this contribution we shall name *Generalized Sturmian Functions* (GSF) those defined in Section 5.1; note that other authors use the same terminology to define a different class of Sturmian functions. One of the advantages of such a method is that it allows to ensure that the continuum wavefunction has the correct asymptotic behavior[22]. To assess the validity of our approach, we will compare the calculated PI cross sections for a number of small molecules with theoretical and experimental data found in the literature.

The rest of this paper is organized as follows. We start with some generalities on PI in Section 2; we continue in Section 3 with a brief panorama of what sort of agreement one observes in the literature between theoretical and experimental cross sections. In Section 4 we present a survey of different theoretical methods used to investigate molecular PI. In Section 5 we introduce the Sturmian approach, and compare our results for PI of H_2O, NH_3 and CH_4 to several theoretical and experimental data.

Atomic units ($\hbar = e = m_e = 1$) are assumed throughout, unless stated otherwise.

2 Generalities

In the study of the interaction of a radiation field (a photon) with a molecular target several processes may occur. Consider a photon of energy $E_\gamma = \hbar\omega$, such that $E_\gamma > I_0$, where I_0 is the ionization potential of the molecule. Once it strikes the polyatomic molecule RA in an initial vibrational state ν_0 (R is the polyatomic radical and A is an individual atom), the different outcomes may be

$$\hbar\omega + \mathrm{RA}\,(\nu_0) \rightarrow \begin{cases} \mathrm{RA}^+ + e^-\,(\ell) & \text{Photoionization,} \\ \mathrm{R}^* + \mathrm{A}^* & \text{Photodissociation,} \\ \mathrm{R}^* + \mathrm{A}^{+*} + e^-\,(\ell) & \text{Dissociative photoionization.} \end{cases} \tag{1}$$

If we have a dissociation process, the final products can be in an excited state. If we have an ejected electron, called photoelectron, it has a defined angular momentum ℓ. In this contribution, we will concentrate only on single PI which can be considered as a "half-scattering" processes. It involves a bound-free transition for which one needs to know only the initial state Ψ_0 of the molecule, usually its ground state (energy E_0), and the final state of the ionized electron. The transition operator, that connects both initial and final states, is described semi-classically via the dipolar approximation; the dipolar operator in both

length (L) and velocity (V) gauges reads

$$\widehat{D}^{(\mathrm{L})} = -\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{r}, \tag{2a}$$

$$\widehat{D}^{(\mathrm{V})} = -\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p}, \tag{2b}$$

where $\hat{\boldsymbol{\varepsilon}}$ gives the polarization of the field. In this work we consider linear polarization along the z direction.

The major task is to calculate accurately the wavefunction Ψ of the photoelectron, that is an electron in a continuum state of the ionized molecular target, with an energy $E = k^2/2$ defined by the energy of the incident photon $E = E_\gamma - I_0$. Such continuum wavefunctions are more difficult to calculate than the low-lying bound-states as they oscillates up to infinity. They are solutions of the time-dependent Schrödinger equation (TDSE) or the time-independent Schrödinger equation (TISE), with well defined properties. They must be regular at the origin of the coordinate system, and the asymptotic boundary conditions are given by the superposition of an incoming-wave Coulomb function plus an incoming spherical wave, generated by the non-Coulomb part of the molecular potential[25]

$$\lim_{r \to \infty} \Psi^{(-)} \propto e^{-i\left(kz + \frac{Z}{k}\ln k(r-z)\right)} + f\left(\hat{k}, \hat{r}\right)\frac{1}{r}e^{-i\left(kr - \frac{Z}{k}\ln(2kr)\right)}, \tag{3}$$

where $f\left(\hat{k}, \hat{r}\right)$ is the transition amplitude and $Z = -1$ for an initial neutral target.

One quantity that is measurable experimentally is the PI cross section, defined theoretically as

$$\frac{d\sigma}{dE} = \frac{\pi e^2}{m^2 \hbar^2 c}\omega^{(\mathrm{g})}\left|\left\langle\Psi_0\left|\widehat{D}^{(\mathrm{g})}\right|\Psi\right\rangle\right|^2, \tag{4}$$

where $\omega^{(\mathrm{L})} = E - E_0$ or $\omega^{(\mathrm{V})} = (E - E_0)^{-1}$ and c is the speed of light.

In most experiments it is difficult to determine the spatial orientation of the molecule in a given laboratory frame. Only a few advanced experimental techniques can perform a full angle-resolved spectroscopy, such as the one based on ultrashort pump-probe laser pulses[26,27] and the full kinematic experiments as COLTRIMS (cold target recoil ion momentum spectroscopy)[28]. In most cases, therefore, one must consider a random orientation of the molecule when it interacts with the radiation field. To do that, two different coordinates systems, whose origin coincide with the center of mass of the target, are considered[29]: the laboratory frame, $\mathbf{r}'$, defined by the polarization axis of the electric field, and a molecular-fixed frame, $\mathbf{r}$, defined by the axis of highest symmetry. Let β and α be the polar angles of this molecular axis with respect to the laboratory frame, and let the set of Euler angles $\hat{\mathfrak{R}} = (\alpha, \beta, \gamma)$ denote hereafter the molecular orientation. A rotation $\hat{\mathfrak{R}}$ will bring the molecular fixed frame into coincidence with the laboratory frame. The dipolar operator in length gauge (2a), for a linearly polarized field (axis z), in the laboratory frame is then

$$z' = \left(\frac{4\pi}{3}\right)^{1/2} r \sum_\mu Y_1^\mu\left(\hat{r}\right)\mathscr{D}_{0\mu}^1\left(\hat{\mathfrak{R}}\right), \tag{5}$$

where $\mathscr{D}_{0\mu}^1\left(\hat{\mathfrak{R}}\right)$ is the rotation matrix[30] that rotates the dipolar operator to the molecular frame. The rotated dipolar operator in velocity gauge follows

a similar expression. In order to calculate a cross section for a randomly oriented molecule, we must calculate first the orientation-dependent transition amplitudes in Equation (4) (see also Section 5.2) and then perform an angular average over $\hat{\mathfrak{R}}$, defined as

$$\int d\hat{\mathfrak{R}} \equiv \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta \int_0^{2\pi} d\gamma\,, \qquad (6)$$

of the square modulus of such transition amplitudes.

3 Examples Taken from the Literature

As mentioned in the Introduction, many different theoretical methods and computational codes have been developed over the years to study PI in multielectron atoms. For molecules, many complications arise. The problem is highly non-central and generally multicenter so that continuum wavefunctions are quite difficult to calculate. Additionally the vibrational structure can have an important influence on the electronic structure and therefore on the PI itself.

To overcome all these complexities, additional to the "traditional" frozen core (FC) or the SEA, one starts to separate the electronic motion from that of the nuclei, and this is done using the BO approximation. One may also implement the fixed nuclei (FN) approximation, and it is possible to go further and use the OCE, where all electrons are referred to a common center, usually the center of mass of the molecule. Such variety of approximations (which are needed to deal with molecular systems), together with the choice of basis functions or adopted numerical approach, translates into a considerable non-uniformity in the quality of the end product. Except for H_2, for most molecules the PI cross sections obtained using different theoretical or numerical methods do not show an overall satisfactory agreement on one hand between them and, on the other hand, with experimental data. This is illustrated below with four different molecules: H_2, N_2, CO_2 and C_6H_6. We emphasize that almost all experimental data presented here do not have explicit error bars, either because they are not indicated in the given references or because they are too small, typically smaller than 3%.

3.1 H_2

We start with H_2, the simplest many-electron molecule. Figure 3.1 shows the PI cross sections obtained using different methods: self-consistent field (SCF, see Section 4.2.1), configuration interaction (CI, see Section 4.1), ground state inversion method (GIPM/D, see Section 4.7.2), random-phase approximation (RPA, see Section 4.9) and logarithmic derivative Kohn method (LDKM, see Section 4.11.1). They are further compared with the experimental data of Chung $et\ al$[31]. For this example, SCF and CI calculations used OCE, CBF used FN and LDKM the FC approximation. Except for the SCF results, we see an excellent agreement between all theories with experimental data. Indeed, the molecule H_2 is sufficiently simple to allow for a PI study taking into account all interactions. One aspect, though, that remains challenging is to calculate precisely the positions and widths of the doubly excited states that depend on the nuclear motion.
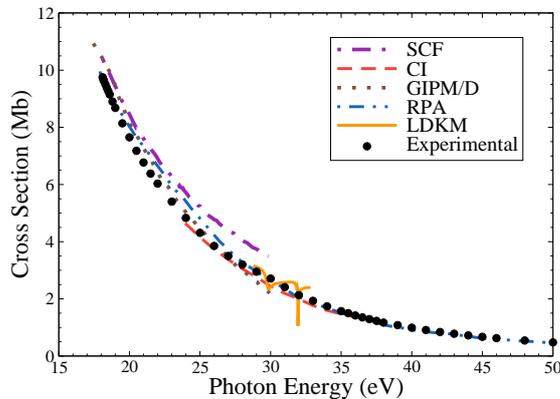
Figure 3.1: (Color online) PI cross section in Mb versus photon energy in eV for the ground state of H_2 molecule. We compare the results obtained using SCF[32] (purple, dash-dot); CI[33] (red, dash); GIPM/D[34] (brown, dots); RPA[35] (blue, dash-dot-dot) and LDKM[36] (orange, solid) with experimental data[31] (black dots).

3.2 N_2

We show in Figure 3.2 the PI cross sections for the outer valence orbital $3\sigma_g$ of N_2. For such MO we show calculations performed with CI (Section 4.1), time-dependent density functional theory (TD-DFT, see Section 4.3.2), multiple-scattering $X\alpha$ (MS $X\alpha$, see Section 4.6), Stieltjes–Tchebycheff technique (STT, see Section 4.10) and iterative–Schwinger method (ISM, see Section 4.12.1). Note that the results for CI and TD-DFT were obtained using OCE, and for ISM using the FC approximation. The theoretical cross sections are compared with the experimental results of Plummer *et al*[37].
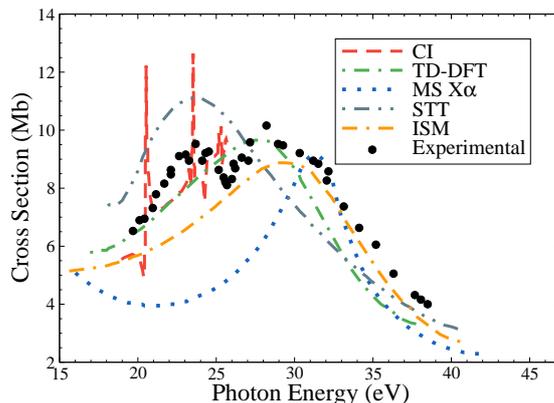
Figure 3.2: (Color online) Partial PI cross section in Mb versus photon energy in eV from the MO $3\sigma_g$ of N_2. Results for CI[38] (red, dash); TD-DFT[39] (green, dash-dot); MS $X\alpha$[40] (blue, dots); STT[41] (gray, dash-dot-dot) and ISM[42] (orange, dash-dash-dot) are compared with experimental data[37] (black dots).

The situation changes drastically when moving from H_2 to a more complex

molecule such as N_2. The Figures show that the agreement between different theories and experimental data is basically lost, especially for energies close to threshold. Moreover, only a partial agreement for higher energies is observed. Except for the CI results, none of the other calculations reproduces the different series of resonances located between 20 and 25 eV.

3.3 CO_2

The PI cross sections for CO_2 are shown in Figure 3.3 for the MO $1\pi_g$. We compare the results obtained with GIPM/D (Section 4.7.2), STT (Section 4.10), ISM (Section 4.12.1) and R-matrix method (RMM, see Section 4.8). The experimental data are taken from Brion and Tan[43].

Here, results for ISM and RMM used both the FC and the FN approximations. Depending on the energy range, the different theoretical calculations present again only a partial agreement, and even if they cannot reproduce completely the experimental data, they perform rather well beyond 25 eV. Although the center of mass of CO_2 is close to the C atom because of its linear geometry, this molecule is particularly difficult to describe: the density of charge is completely delocalized around the molecule and only the use of multicenter wavefunctions yields acceptable PI results, as in the GIPM/D case.
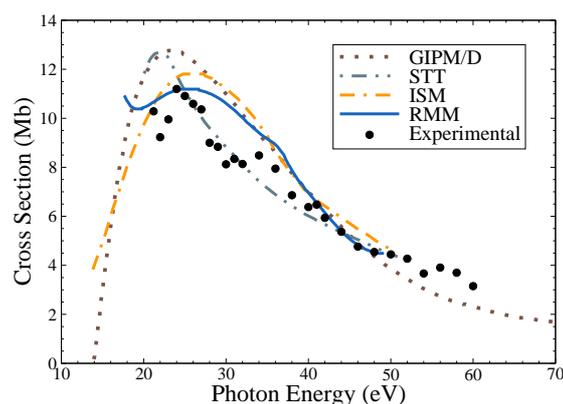
Figure 3.3: (Color online) Partial PI cross section in Mb versus photon energy in eV from the MO $1\pi_g$ of CO_2. Results for GIPM/D[44] (brown, dots); STT[41] (gray, dash-dot-dot); ISM[45] (orange, dash-dash-dot) and RMM[46] (blue, solid) are compared with experimental data[43] (black dots).

3.4 C_6H_6

Finally, for benzene (C_6H_6), PI cross sections for the outer valence orbital $1e_{1g}$ are shown in Figure 3.4. The theoretical results obtained using DFT (Section 4.3.1), TD-DFT (Section 4.3.2), GIPM/D (Section 4.7.2) and LDKM (Section 4.11.1) are compared with the experimental data by Carlson *et al*[47].

This is a rather complex molecule to describe theoretically, and the difficulties show up in the PI spectra. None of the calculations reproduce accurately the resonances (neither their energy position nor their intensity), let alone the overall cross section magnitude except at rather high photoelectron energies.
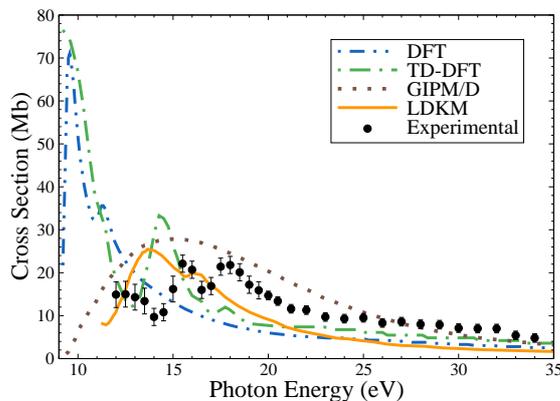
Figure 3.4: (Color online) Partial PI cross section in Mb versus photon energy in eV from the MO $1e_{1g}$ of C_6H_6 (benzene). Results for DFT[48] (blue, dash-dot-dot); TD-DFT[49] (green, dash-dot); GIPM/D[50] (brown, dots) and LDKM[51] (orange, solid) are compared with experimental data[47] (black dots).

As evidenced from Figures 3.1 to 3.4, except for H_2, for all other molecules we can draw similar conclusions: (1) large disagreements between methods are clearly observable when comparing PI cross sections; (2) experimental data, in particular near threshold, are generally not well reproduced (other features of the continuum spectra are also difficult to reproduce). This is also true for H_2O, NH_3 or CH_4 molecules; the cross sections will be presented in Section 5.3, where we shall compare different theoretical calculations including ours obtained with the Sturmian approach. To have an overview of most methods that have been proposed to describe molecular PI, we present in the next section a survey and indicate to which molecules they have been applied (a rather complete list is presented in Appendix A).

4   Survey of Theoretical Methods

4.1   CI

One of the "classical" methods used to study electronic structure in atoms and molecules is configuration-interaction (CI); a description of its use for the study of PI of molecules can be found in Reference 52.

Some results obtained using the CI method are the studies by Daasch *et al*[53] for CO_2, van Dishoeck *et al*[54] for HCl and Decleva *et al*[55] for O_3. Using B-splines[56] as a basis set, Apalategui and Saenz[57] studied multiphoton ionization of H_2; Vanne and Saenz[58] studied HeH^+; Fojón *et al*[59] also studied H_2; Sanz–Vicario *et al*[33] studied PI of H_2 by ultrashort laser pulses and Sansone *et al*[27] for H_2 and D_2; Dowek *et al*[60] studied circular dichroism in H_2. Using the so-called time-dependent CI[61], we find the works of Klinkusch *et al*[62] for LiCN, and of Sonk and Schlegel[63] for C_4H_6 (butadiene). Finally, using the multichannel CI complete-active-space[64], we can find the works of Stratmann *et al*[38] for N_2, and of Stratmann and Lucchese[65] for O_2.

4.2 Hartree–Fock Methods

4.2.1 Self-Consistent Field

Among the studies that have used the Hartree–Fock (HF) method and the self-consistent field (SCF) to study PI of molecules, we find the work of Dalgarno[66] for CH_4; Kelly[32] studied H_2; Schirmer et al[67], together with the Green's function formalism, studied the inner-valence PI of N_2 and CO; Padial et al[1], using Gaussian-type orbitals (GTOs), studied C_2. For calculations performed with the relaxed-core HF approximation, we have the results of Larkins and Richards[68] for Li_2; the studies of Saito et al on the K-shell photoelectron angular distribution from CO_2[69] and from NO_2[70]; Semenov et al[71] studied the PI from the K-shell of the CO. We should also mention the review of different applications of SCF by Ågren et al[72].

4.2.2 Multiconfiguration time-dependent Hartree–Fock

In general, it is difficult to describe with high precision highly excited states and non-adiabatic dynamics in molecules, especially if one is interested in studying ionization by high-intensity radiation fields. The multiconfiguration time-dependent Hartree–Fock (MCTDHF) approach is a method that uses a linear combination of determinants of time-dependent orbitals, and is flexible enough to describe the response of a molecule to short and intense laser pulses. The formalism can be found in References 73–75.

The MCTDHF has been used by Kato and Kono[75] and by Haxton et al[76] to study PI of H_2 by intense laser fields, and also by Haxton et al[77] for HF.

4.3 Density Functional Theory

The density functional theory (DFT) is widely used in quantum chemistry. It allows to determine easily the electronic structure of a given system (an atom, a molecule, a crystal, etc), regardless of its extension or the number of particles that constitute it. While "standard" quantum mechanics works directly with the many-body wavefunctions of the different particles in a given system, the DFT uses the one-electron electronic density $n(\mathbf{r})$, and is based on two theorems, called the Hohenberg–Kohn theorems[78]. In different implementations of the DFT to study PI of molecules, $n(\mathbf{r})$ is calculated using a conventional linear combination of AOs (LCAO)[48].

4.3.1 Kohn–Sham DFT

In the Kohn–Sham DFT (KS DFT)[79], the Hamiltonian of the molecular system is determined by the density of the occupied orbitals in the ground state, and in terms of the Hartree potential, the electron-nuclei interaction, and the so-called exchange-correlation potential which contains all the "unknowns" of the system. Different potentials are available in the literature for different atomic and molecular systems (see, for instance References 80 and 81), based, for example, in the local density approximation or in the generalized gradient approximation.

The KS DFT has been used by Venuti et al[48] to study PI in C_6H_6; by Stener and Decleva, using the OCE approximation, to study HF, HCl, H_2O, H_2S, NH_3 and PH_3 (Reference 82), and CH_4, SiH_4, BH_3 and AlH_3 (Reference

83). Toffoli *et al*[84], using the multicenter expansion, calculated cross sections for Cl_2, $(CO)_2$ and $Cr(CO)_6$. Woon and Park[85] also studied C_6H_6 (benzene), $C_{10}H_8$ (naphthalene), $C_{14}H_{10}$ (anthracene) and $C_{16}H_{10}$ (pyrene). Stranges *et al*[86] studied the dynamics in circular dichroism of the C_3H_6O (methyl-oxirane). Toffoli *et al*[87] studied the PI dynamics in $C_4H_4N_2O_2$ (uracil).

4.3.2 *Time-Dependent DFT*

The time-dependent DFT (TD-DFT)[88] constitutes another line of development of the DFT methods. In the first order time-dependent perturbative scheme, where the zeroth order is equivalent to the KS DFT[89], the linear response of the electronic density $n(\mathbf{r})$ to an external weak time-dependent electromagnetic field can be described by a SCF potential, given by Zangwill and Soven[90].

The TD-DFT has been used by Levine and Soven[39] to calculate photoe-mission cross sections and asymmetry parameters of N_2 and C_2H_2. Stener, Decleva and coworkers, using B-splines[56] and the OCE, studied PI for different molecules: Stener and Decleva[89] calculated the cross sections for N_2 and PH_3; Stener *et al*[91] for CH_4, NH_3, H_2O and HF; Stener *et al*[92] for CO and also from the K-shell[93]; Fronzoni *et al*[94] for C_2H_2; Stener *et al*[49] for CS_2 and C_6H_6; Toffoli *et al*[95] and Patanen *et al*[96] for CF_4, and Holland *et al*[97] for pyrimidine and pyrazine. We also find the work of Russakoff *et al*[98] for C_2H_2 and C_2H_4, and by Madjet *et al*[99] for C_{60}. Different results for molecular PI have been reviewed by Stener *et al*[100].

For the sake of completeness, we also mention some studies of molecular PI that use a slightly different approach, the static-exchange DFT: Plésiat *et al*[101] investigated PI of N_2 and CO, and Kukk *et al*[102] from the inner-shells of CO.

4.4 Complex Methods

4.4.1 *Complex Scaling*

The complex scaling (CS) method[103,104] has been used extensively to study ionization and, mainly, resonance phenomena in atoms and molecules. The idea behind this method is to scale the coordinates of all particles in the Hamiltonian by a complex-valued scale factor: $r \to re^{i\theta}$. One variant of the CS is the so-called exterior complex scaling (ECS)[105–107], whereby the coordinates scale only outside a fixed radius R_0

$$r \to R(r) = \begin{cases} r & \text{for } r \leqslant R_0, \\ R_0 + (r - R_0)e^{i\theta} & \text{for } r > R_0. \end{cases} \tag{7}$$

The ECS method has been applied to study general scattering problems using L^2 basis set representations. It is especially well suited to study ionization processes in molecules, since the definition of the exterior scaling (7) avoids complicated scaling expressions in the nuclear attraction terms of the Hamiltonian[106] when R_0 is large enough to enclose all the molecular nuclei.

The ECS has been used mainly by McCurdy, Rescigno, Martín and coworkers to study different ionization processes in atoms and molecules: McCurdy and Rescigno[108,109] used Cartesian Gaussian-type orbitals (CGTOs) to calculate PI cross sections of H_2^+; Vanroose *et al*[110,111], using B-splines[56], studied double PI (DPI) of H_2; Rescigno *et al*[112] performed *ab initio* DPI calculations of H_2;

Tao *et al*, using discrete variable representation (DVR)[113], calculated PI cross sections for H_2^+ [114,115] and angular distribution for DPI of H_2 [116].

4.4.2 Complex Basis Functions

In the complex basis functions (CBF) technique[108,109,117] (the CS method can be considered a particular case of the CBF where the basis functions are defined in terms of the physics of the problem) the continuum scattering information is extracted from a finite-matrix representation of the electronic Hamiltonian in a set of complex square-integrable basis functions. The resulting matrix elements necessary to obtain the cross section, can be calculated efficiently using a discrete basis set approximation to the spectrum of the Hamiltonian[108].

The CBF technique, together with complex GTO, has been used by McCurdy and Rescigno[108] to calculate PI cross section of H_2^+; by Yu *et al*[117] for valence- and K-shell ionization of N_2, and by Morita and Yabushita[118] for H_2^+ and H_2.

4.5   Linear Algebraic Method

The linear algebraic method (LAM), developed by Collins and Schneider[119,120], has been applied successfully to study molecular excitation and ionization by electron collisions. The adaptation of the method to study PI in molecules is given explicitly in Reference 121. The LAM presents the advantage of including explicitly an effective optical potential in order to introduce correlation effects into the scattering solution[121].

While the initial state is treated separately, usually in terms of GTO or CGTO[119], the method is used to calculate directly the ejected electron unbound wavefunction that satisfies the TISE. To do so, the configuration space is divided into two regions, with the boundary at $r = a$: (1) for $r \geqslant a$, where nonlocal effects are negligible, the wavefunction can be calculated by standard propagation procedures; (2) for $r < a$, where exchange and correlation effects are important, the wavefunction is expanded in two terms: one as a linear combination of the wavefunctions of the molecular-ion target and the scattering wavefunction, and the other in a set of "correlation" functions that are added for completeness[121].

In the LAM one obtains a set of differential equations in the SEA, that can be converted into a set of radial integro-differential equations using an expansion in partial waves of the electronic wavefunctions. Then, this set of scattering equations is further transformed into a set of coupled integral equations using Coulomb Green's functions[119]. Finally, by introducing a discrete quadrature to evaluate the integrals, one obtains a set of linear-algebraic equations that can be solved with standard linear systems routines. This solution must be matched at $r = a$ with the result of the propagation scheme to the asymptotic region. More details on the effective optical potential are given in the References 121, 119 and 122.

To our knowledge, this method has been used only by Collins and Schneider[121] to calculate cross sections for H_2, N_2, NO and CO_2.

4.6 Multi-Scattering

The multiple-scattering method (MSM) has been developed in different physics fields, as in nuclear physics[123], solid state physics[124], and also in atomic and molecular physics (see, for example, References 125 and 126, and references therein). The idea behind the MSM is to represent the molecular field, that in general is highly non-central in the molecular core region, by a set of three potentials V_I, V_{II} and V_{III}, defined in different non-overlapping spheres (called muffin-tin partitioning): (I) defined by the $\{I_i\}$ spherical regions containing the different atomic nuclei at their center $r_i = 0$, and with radii $\{\rho_i\}$; (II) defined by $r_i > \rho_i$ and $r_0 < \rho_{III}$, where r_0 is the radial coordinate from the center of the molecule and ρ_{III} is the outer sphere radius, measured from the molecular center. In general, the potential V_{II} is considered constant; (III) defined by $r_0 \geqslant \rho_{III}$. The potential V_{III} has a spherical symmetry. One can construct the photo-electron continuum wavefunction taking into account the continuity conditions between all three regions, and imposing the incoming boundary conditions (3) in the external region. The total wavefunction is written as $\Psi = \sum_i \Psi_i + \Psi_{II} + \Psi_{III}$, where each term is a solution to the potential of the corresponding region of the molecular field, and obeys the adequate asymptotic boundary conditions.

The MSM or, equivalently the multiple-scattering with an undetermined factor α (MS Xα)[127], have been widely used to study ionization of molecules by photon and electron impact. For example, Davenport calculated cross sections for N_2 and CO[40,128], and for H_2[128]; Dehmer and Dill calculated the K-shell PI of N_2[129]; Grimm[130] calculated the cross section for C_2H_4 and Grimm *et al*[131] for N_2, CO, CO_2, COS and CS_2; Rosi *et al*[132] studied PI in CH_4 and CF_4; Tse *et al*[133] investigated the photoabsorption spectra in $SiCl_4$; Ishikawa *et al*[134] studied, implementing a DVR[113] method, SiH_4, SiF_4 and $SiCl_4$; Powis studied PI in PF_3[135], CH_3I[136] and CF_3Cl[137]. Finally, Jürgensen and Cavell[138] compared directly experimental results with the MS Xα for NF_3 and PF_3.

4.7 Plane-Wave-Based Methods

4.7.1 Plane-Wave and Orthogonalized Plane-Wave Approximations

The simplest description of an ionized electron is the plane-wave approximation (PWA), but it is not expected to give accurate results near threshold[139]. To our knowledge, the first implementations of the PWA are due to Kaplan and Markin[140,141], Lohr and Robin[142], and to Thiel and Schweig[143,144].

The final state of the molecule describes one electron that has been ex-cited from a given initial MO to a continuum normalized plane-wave orbital[139]. This plane-wave is not necessarily orthogonal to any of the occupied MOs; if orthonormality is imposed, we have the orthogonalized PWA.

The PWA and the orthogonalized PWA, together with Slater-type orbitals (STOs) to describe AO, have been used by Rabalais *et al*[145] and by Dewar *et al* [146] to calculate PI cross sections for H_2, CH_4, N_2, CO, H_2O, H_2S and H_2CCH_2. Huang *et al*[147] used the orthogonalized PWA to calculate angular asymmetry parameters for H_2, N_2 and CH_4. Beerlage and Feil[148] calculated cross sections for HF, $(CN)_2$, $CaHCN$, $C_2(CN)_2$, N_2, CO, H_2O, furan, pyrole and tetrafluoro-pyrimidine. Schweig and Thiel[149] calculated the relative band intensity of N_2, CO, H_2O, H_2S, NH_3, PH_3, CH_4, $(CH_3)_2S$, C_6F_6, among others.

Hilton *et al*[150] have used the so-called effective PWA to calculate cross sections for H_2, CO, H_2O and C_2H_4. Finally, Deleuze *et al*[151] used the orthogonalized PWA, together with a many-body Green's function framework, to calculate PI cross sections for CH_4, H_2O, C_2H_2, N_2, and CO.

4.7.2   Ground Inversion Potential Method

The so-called ground state inversion potential method (GIPM) has been developed by Hilton, Hush, Nordholm and coworkers[150,152] with the aim of obtaining a chemical theory of PI intensities[153]. This method uses the standard one-electron PWA, the orthogonalized PWA or the energy shifted PWA[150] in order to calculate the electronic continuum final wavefunction. The cross section is obtained from an atomic summation theory together with a plane wave analysis of diffraction effects from photoelectron amplitudes from different atoms that interfere with each other[34,153]. The main difference of GIPM with a standard PWA is that the potential felt by an electron when leaving an atomic center in a molecule is calculated directly by inversion of the ground state HF orbital[152,153]. The GIPM theory can include three important effects: the change in the nature of the atomic orbitals upon formation of the molecule, diffraction effects[153] and exchange in an exact way.

The GIPM has been used by Hilton *et al* to calculate PI cross sections for H_2O[154] and for H_2, N_2 and CO[34]. Also Kilcoyne *et al* calculated cross sections for H_2, HF and N_2[153]; H2O, NH_3 and CH_4[155]; CO, CO_2 and N_2O[44], and for C_2H_4 and C_6H_6[50].

4.8   *R*-Matrix Method

Originally introduced in nuclear physics, the *R*-matrix method (RMM) has been adapted to atomic and molecular physics by Burke and coworkers (see Reference 156 and references therein). Applications of this method, in particular for electron collisions, have been reviewed elsewhere[157–159]. The idea behind the RMM is to enclose the scattering particles and the target within a sphere of radius a, so that it should be possible to characterize the system using the eigenenergies and the eigenstates computed within the sphere. Then by matching them to the known asymptotic solutions, one can extract all the scattering parameters. The *R*-matrix is defined as the matrix that connects the two regions in which the space is divided into. They are: (1) an internal region, where all the particles are close to one another, so that the short-range interactions and exchange are important; (2) an external region, where all particles are still interacting, but the forces are direct and could have a multi-polar character. In the most conventional use of the RMM, the Hamiltonian of the internal region is diagonalized in order to obtain the *R*-matrix eigenenergies and eigenfunctions, generally using the non-adiabatic formalism[160]. The initial and final states are expanded in terms of these eigenstates. The corresponding coefficients for the initial state are usually obtained by performing an all-channels-closed scattering calculation, and in this case the problem is reduced to find the zeros of a determinant[161,162]. To obtain the coefficients for the final state, calculations of electron scattering by the corresponding molecule can be performed, and the resulting *R* matrices represent the result of a full non-adiabatic treatment of the internal region of the scattering problem[159], and provides the solution in the external region[163].

Finally, with both sets of coefficients, it is possible to calculate the required transition dipole moments, and thus the PI cross section (4).

Since the corresponding formalism is relatively new, the RMM has not been used for molecules as much as for atoms. However, we have the works by Tennyson et al[164] for H_2, and by Tennyson[165] for H_2 and D_2. The so-called R-matrix Floquet theory[166,167] has been used by Burke et al[167] and by Colgan et al[168] to study multiphoton processes in H_2. Saenz[169], using STOs, studied PI in HeH^+. Tashiro[170] calculated cross sections for N_2 and NO. Finally, Harvey et al[46] recently studied CO_2, using GTOs combined with Coulomb and Bessel functions.

4.9   Random Phase Approximation

The random phase approximation (RPA) is a method that has been applied with success to study PI in atoms and molecules[171,172]. One advantage is that PI cross sections calculated in length or velocity gauges coincide. Additionally, the computational effort required in the RPA implementation is comparable to calculations in the single active electron (SAE) approximation, since the RPA uses only two-electron integrals involving two occupied and two unoccupied orbitals[173,174].

In the standard procedure of the RPA, the ground state and the one-electron wavefunctions for the excited and continuum states of the molecule are calculated at HF level. With these, all required matrix elements and in particular the Coulomb and dipole matrix elements, can be calculated directly. Next, the RPA dipole matrix elements are calculated solving the corresponding equation, and the results are used to obtain directly PI cross sections or the required observables[173–176].

The RPA has been used to study PI of H_2 by Martin et al[35], by Schirmer and Mertins[177] and by Semenov and Cherepkov[176,178]. For N_2 we can find calculations performed by Lucchese and Zurales[179]; by Semenov and Cherepkov[175,180]; by Yabushita et al[174], using complex functions; and by Montuoro and Moccia[181], using mixed L^2 basis sets (STOs and B-splines[56]). For H_2S we have the results of Cacelli et al[182]. For LiH, calculations were performed by Carmona–Novillo et al[183]. For C_2H_2 we have the results of Yasuike and Yabushita[184], who used complex basis functions (see Section 4.4.2), and by Montuoro and Moccia, using the mixed L^2 basis sets. We can find also calculations for the K shell of N_2 by Cherepkov et al[185]; for the ion C_{60}^+ by Polozkov et al[186], or for the fullerenes C_{20} and C_{60} by Ivanov et al[187]. Extensive calculations have been performed by Cacelli et al[188], to study PI in CH_4, NH_3, H_2O and HF, and by Amusia et al[171], who used the RPA with exchange to calculate PI cross sections of CH_4, C_2H_6, C_3H_8, C_2H_4, C_2H_2, NH_3, H_2O, CN^-, N_2, CO, CO_2, N_2O and NO_2^-.

4.10   Stieltjes–Tchebycheff Technique

The Stieltjes–Tchebycheff technique (STT), developed by Langhoff and coworkers (see, for example, References 189 and 190 and references therein), is based on theorems from the theory of moments[191]; its flexibility allows the use of different type of basis sets[190,192,193]. The technique has been widely and successfully used to study ionization processes in different atomic and molecular

systems.

The strength of the interaction of unpolarized radiation with a target gas can be described by Kramers–Heisenberg expression of the polarizability (frequency-dependent) of the constituent molecules. This strength can be written as a Stieltjes integral over the appropriate oscillator strength distribution[189,193] or, alternatively, by the use of the cumulative oscillator-strength distribution which can be approximated by an histogram (Stieltjes procedure). Even if such an histogram cannot represent adequately the continuum of the molecule, it can give good approximations to the related power moments, and it rigorously bounds the correct distribution through Tchebycheff inequalities[191]. More technical details about the direct computational implementation of the STT are provided in Reference 190.

The STT has been used to study PI in CH, using STOs, by Barsuhn and Nesbet[194]; in H_2, using GTOs in a CI method (see Section 4.1), by ONeil and Reinhardt[195]; in N_2, together with GTOs, by Rescigno et al[193] and using LCAO with optimized STOs by Stener et al[41]. In H_2O by Williams et al[196] and by Delaney et al[197] in the SEA, both using GTOs; by Diercksen et al[198], using Cartesian Gaussian basis sets and by Cacelli et al[199] using STOs in the independent-channel approximations. By Cacelli et al, we also find calculations for NH_3[199], HF[200], HCl[201], H_2S[202] and CH_4[200]. For CO we mention the work by Görling and Rösch[203], who used GTOs. For F_2, Orel et al[204] used contracted Gaussians. For C_6H_6 Gokhberg et al[205] used the STT together with the Lanczos algorithm. Finally, Stener et al[41] have performed calculations using LCAO with optimized STOs for CO_2, N_2O, SF_6, C_2N_2, $TiCl_4$ and $Cr(CO)_6$.

4.11   The Kohn Variational Method

Among different approximate methods used to determine the energy spectra and the corresponding wavefunctions, we have the perturbation theory and the standard Ritz variational method[25], where approximate solutions of the TDSE or the TISE for a given problem are found in a subspace of the real problem. Besides the standard Ritz method, there is also, e.g., the Kohn variational method (KVM)[206]. The idea behind the latter is to find a variational expression that allows one to calculate the wavefunction with a correct asymptotic behavior. This is dictated by two arbitrary $f_\ell(r)$ and $g_\ell(r)$ functions, that behave asymptotically as the regular $F_\ell(kr)$ and, respectively, irregular $G_\ell(kr)$ Coulomb functions. The trial wavefunction can be written as

$$\psi_\ell^{\mathrm{t}}(r) = f_\ell(r) + \lambda^{\mathrm{t}} g_\ell(r) + \sum_i c_i \varphi_i(r), \qquad (8)$$

where $\{\varphi_i\}$ is a set of L^2 functions and λ^{t} is a trial parameter. The Kato identity[207] is used to find a stationary λ^{s} value. We can distinguish two options for the trial wavefunction (8): (1) if f_ℓ and g_ℓ are the regular and irregular Coulomb functions, then we have $\lambda = \tan\delta_\ell$, where δ_ℓ is the phase shift related to a short range potential; (2) if g_ℓ is an outgoing function $h_\ell^{(-)}$, called "regularized" irregular Coulomb function (defined as $h_\ell^{(-)}(r) = ik^{-1/2}[F_\ell(kr) - ic(r)G_\ell(kr)]$, where $c(r)$ is a cutoff function) then $\lambda = e^{i\delta_\ell}\sin\delta_\ell$, i.e., the T-matrix (transition matrix). In this case we have the complex Kohn method[207,208].

Two different implementations of the KVM in the study of PI of molecules are separately hereafter described.

4.11.1   Logarithmic Derivative Kohn Method

The logarithmic derivative Kohn method (LDKM)[209,210], and its variant, the finite-volume variational method[211], were originally proposed to generate a translational basis for reactive scattering, using Lobatto shape functions[210,212,213]. In this method, all the required radial integrals are performed explicitly over a finite volume V, usually a sphere. The main difference between the LDKM and the standard KVM is that different coefficients are added to the functions f_ℓ and g_ℓ in (8); these coefficients can be determined by matching the wavefunction and their derivatives with the exact Coulomb functions across the surface that delimits the integration volume V[51,213]. In many of the implementations of the LDKM, Lobatto shape functions, referred usually as free-type functions, are used as the basis set $\{\varphi_i\}$ in (8).

The LDKM has been used to calculate PI cross sections for H_2^+ by Le Rouzo and Raşeev[211], and by Rösch and Wilhelmy[213]; Raşeev[36] studied autoionization in H_2; and Wilhelmy $et\ al$[51,214] calculated cross sections and asymmetry parameters for N_2, CO and C_6H_6.

4.11.2   Complex Kohn method

The complex Kohn method (CKM), developed by McCurdy, Rescigno and coworkers to study excitation and ionization of molecules by electron collisions[208,215,216], have proved to be very effective, in particular in the first-order calculation of dipolar transition moments[215]. The adaptation of the method to study PI in molecules has been described by Lynch and Schneider[217]. Different elections of the arbitrary cutoff function $c(r)$ or the irregular function $g_\ell(r)$ have been tested[217,218].

The CKM has been used Lynch and Schneider[217] to study PI of H_2 and N_2; by Rescigno $et\ al$[219] to study CO, examining the effects of the interchannel coupling; Orel and Rescigno[220] to study NH_3 and, more recently, Jose $et\ al$[221] to study PI of SF_6 also adding interchannel coupling effects.

4.12   The Schwinger Variational Method

While many variational methods are based on the TISE (a differential equation), several others, as the Schwinger variational method (SVM)[222] are based on the equivalent integral equation, the Lippmann–Schwinger equation (LSE)[223,224].

The advantage of the LSE over the TISE to study collisions processes is that the correct boundary conditions of the problem are automatically incorporated through the use of the corresponding Green function G^C. The SVM is a powerful formulation of the scattering problem that can provide highly accurate solutions without requiring expansions in very large basis sets[225,226]. The idea behind this method is to obtain a stationary variational condition over the T-matrix. In general, one can obtain better converged results using the SVM compared to the KVM results.

The implementation of the SVM has been developed along two methods, named the Schwinger multichannel method[227] and the iterative-Schwinger method (ISM). The latter, and a variant using continued fractions, are now briefly described.

4.12.1 Iterative Schwinger

The ISM is an iterative approach to the solution of collisions problems using the SVM[225] to solve the LSE. The first implementation of ISM[226,228,229] was the study of scattering of low-energy electrons by atoms and molecules. In the case of molecules, the fixed-nuclei approximation was used together with the assumption that the interaction between the ionized electron and the molecular ion is described by the static-exchange potential[229,230]. The description of the ISM implementation to study PI is given with details in References 42 and 45.

In the ISM instead of solving the associated LSE for each partial-wave of the scattering function, one solves equivalently a LSE for the T matrix[225,230]: $T = U + UG^{\mathrm{C}}T$. The iterative method begins by approximating the short-range potential U by a separable potential $\widetilde{U}$, using an initial set of expansion functions R; then the scattering solutions for the approximate potential $\widetilde{U}$ are obtained from the corresponding LSE. The iterative procedure is continued by augmenting the original set of functions with those obtained with the approximated potential. Using this augmented set of functions, the first iteration is completed by calculating a new T matrix. A second iteration is begun by constructing a new set of solutions and combining them with the initial trial functions set; this will yield a new T matrix. The iterative procedure is continued until the wavefunctions converge, yielding the LSE solutions for the exact potential U[229,230].

This method has been widely used to study PI of molecular systems. Using CGTO as the initial set of functions R, we find calculations by Lucchese $et\ al$[42] for N_2; using spherical GTOs, Lucchese $et\ al$[45,230] calculated PI cross section for CO_2 and Lynch $et\ al$[231] for C_2H_2. Natalense $et\ al$ presented results for SF_6[232] and for CH_4, CF_4 and CCl_4[233]; Machado $et\ al$ for H_2O[234] and SiH_4[235]; Machado and Masili[236] studied H_2; Stephens and McKoy[237] for OH; Braunstein $et\ al$[238] for CH_4; Wells and Lucchese[239] for C_2H_2; for C_{60} we find the results by Gianturco and Lucchese[240]; and Wiedmann $et\ al$[241] calculated the rotationally resolved PI cross section for CH_3, H_2O, H_2S and H_2CO.

4.12.2 Continued Fractions

The method of continued fractions (MCF) was originally proposed by Horáček et Sasakawa[242,243] for the study of elastic scattering of fast electrons by atoms; subsequently, Lee $et\ al$ adapted it to study scattering of slow electrons by atoms[244] and by linear molecules[245], and extended it to study ionization by electron collisions in polyatomic molecules[246,247]. The extension of the MCF to the PI study of molecules is explained with details in Reference 248. The idea is to represent the scattering matrix as a continued fraction. The continuum wavefunction is obtained from the solution of the LSE using the static-exchange potential, with the long-range Coulomb potential of the ionic core removed. The MCF does not require basis functions and it is characterized by rapid convergence.

The application of the MCF starts with the definition of a nth-order weakened potential operator $U^{(n)}$, from which the reactance matrix $\mathbf{K}$ is expressed in the form of a continued fraction. The nth-order correction to $\mathbf{K}$, as well as to the wavefunction, can be approximated successively. The operator $U^{(n)}$ becomes weaker and weaker as n increases, and the procedure can be stopped after a few steps. The converged $\mathbf{K}$ matrix corresponds to the exact solution

for a given potential U in LSE[248].

To our knowledge, the MCF has been used only to study PI of NH_3[248].

4.13   Crank–Nicolson

The Crank–Nicolson (CN) method[249] was originally developed to solve numerically differential equations of heat-conduction type, employing a combination of backward/forward finite-difference of all involved variables. It is correct up to the second order in $\widehat{H}\Delta t$, and is numerically stable. The CN scheme can be used to propagate an initial wavefunction with an imaginary time evolution operator, in which, by the Wick rotation, the time t is replaced by $-i\tau$. In such a way, any initial arbitrary state can converge directly to a particular desired state (bound or continuum), just by adjusting the time-step of the propagator.

The CN scheme has been used to study general PI features by Goldberg and Shore[250]; we can find also different studies in PI of H_2^+ by Picón et al[251], Yuan et al[252], Silva et al[253] and Bian[254]. The ion HeH^{2+} has been studied by Bian[254] and the angular distributions for H_2 by Yuan et al[252].

5   Sturmian Approach

5.1   Generalized Sturmian Functions

In the literature we can find different approaches to Sturmian functions, depending on the type of problem to be solved. There are essentially two lines, one associated to bound states and another to scattering problems. The first line initiated by Shull and Löwdin[255], formalized by Goscinski[256] and impulsed later on by Aquilanti and coworkers[257,258]. It is within this line that the generalized Sturmian functions were introduced by Avery and coworkers[259,260] to deal with many electron atoms and chemical systems. On the scattering line, the work was initiated by Rawitscher[261,262] and continued by Macek, Ovchinnikov and coworkers[263,264]. We extended the scattering functions proposed by Rawitscher and started to use them in scattering studies with the name Generalized Sturmian Functions (GSFs) to indicate that the basis functions are solving general atomic potentials.

Details about the presently used GSF are given in References 22 and 23 and references therein, and only the essentials are recalled here. GSF are solutions of a Sturm-Liouville problem, from which Rotenberg took the name. Noted $\mathcal{S}_n^{(\ell,\,E)}(r)$, they are regular at the origin and satisfy the two-body non-homogeneous Schrödinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell\,(\ell+1)}{2r^2} + \mathcal{U}\,(r) - E\right]\mathcal{S}_n^{(\ell,\,E)}(r) = -\beta_n^{(\ell,\,E)}\mathcal{V}\,(r)\,\mathcal{S}_n^{(\ell,\,E)}(r), \quad (9)$$

where E is an externally fixed parameter and $\beta_n^{(\ell,\,E)}$ are the eigenvalues for a given angular momentum ℓ. In general, the generating potential $\mathcal{V}\,(r)$, a short-range potential, dictates the size of the inner region in which most of the dynamics is supposed to occur, while the auxiliary potential $\mathcal{U}\,(r)$ determines the asymptotic behavior of all GSFs. This property is illustrated in Figure 5.1, for functions with a fixed energy $E = 0.5$ a.u., an auxiliary Coulomb potential with

charge $Z = -1$ and a Yukawa generating potential. In general, the outgoing asymptotic behavior of the GSFs with an auxiliary Coulomb potential is given by the second term of (3)

$$\lim_{r \to \infty} \mathcal{S}_n^{(\ell, E)}(r) \propto e^{i\left(kr - \frac{Z}{k} \ln(2kr)\right)}. \tag{10}$$

Additionally, all the solutions conform a complete basis set, with the potential-weighted orthogonality relation

$$\int_0^\infty dr \, \mathcal{S}_{n'}^{(\ell, E)}(r) \, \mathcal{V}(r) \, \mathcal{S}_n^{(\ell, E)}(r) = \delta_{n'n}. \tag{11}$$

Note that the integral is defined without taking the complex conjugate of the function $\mathcal{S}_{n'}^{(\ell, E)}(r)$.
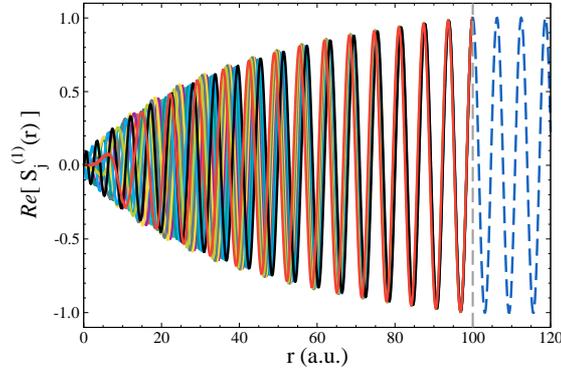
Figure 5.1: (Color online) Real part of 10 generalized Sturmian functions, with a fixed energy $E = 0.50$ a.u. and $\ell = 1$, obtained solving Equation (9), for $r \in [0, 100]$, together with a Coulomb auxiliary potential with charge $Z = -1$, and a Yukawa potential as a generating potential, with parameter $\alpha_{\text{short}} = 0.0219$. The exact Coulomb (analytic) regular function (blue, dash) is also shown.

5.2 Sturmian Approach to Photoionization Process

We shall present in this section the theoretical formalism developed within a Sturmian approach for molecules. We start with a brief description of the used molecular model potentials, then we derive the driven equation of the TISE and provide the necessary formula to calculate the PI cross section. As a simple illustration of the numerical implementation in the atomic case, we show results for the hydrogen atom.

5.2.1 Molecular Model Potentials

To study PI of molecules, we shall use the SAE approximation[265] for the initial state wavefunction. We then need a molecular model potential that plays the role of a scattering potential. Consider the active electron placed in the MO i of the ground state, and denote $\phi_i(\mathbf{r})$ the corresponding wavefunction. The

molecular model potential we shall use is the following[266]

$$V_{i\,\mathrm{mol}}\left(\mathbf{r},\mathbf{R}\right) = -\sum_{n=1}^{M} \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|} + \sum_{j=1}^{N_{\mathrm{MO}}} N_{ij} \int d\mathbf{r}' \frac{|\phi_j\left(\mathbf{r}\right)|^2}{|\mathbf{r}-\mathbf{r}'|}, \tag{12}$$

where M is the number of nuclei in the molecule, Z_n is the charge of each nucleus, $\mathbf{R}_n$ is the position of each nuclei respect to the center of mass of the molecule, N_{MO} is the number of MOs and $N_{ij} = 2 - \delta_{ij}$. This potential is the direct term within the SEA. For the sake of simplicity, the $\mathbf{R}$ dependence is omitted hereafter.

We shall take the MO i given by Moccia; they are expressed as

$$\phi_i\left(\mathbf{r}\right) = \sum_{j=1}^{N} A_{ij} \mathcal{R}_j\left(r\right) S_{\ell_j}^{m_j}\left(\hat{r}\right), \tag{13}$$

where $S_{\ell_j}^{m_j}\left(\hat{r}\right)$ are the real spherical harmonics[30], and the N radial wavefunctions are given as Slater type-orbitals (STOs)

$$\mathcal{R}_j\left(r\right) = \left[\frac{(2\zeta_j)^{2n_j+1}}{(2n_j)!} \right]^{1/2} r^{n_j-1} e^{-\zeta_j r}, \tag{14}$$

with tabulated integers n_j and exponents ζ_j. These MO allow one to calculate analytically, in a partial-wave expansion, the molecular model potential.

As mentioned before, in a typical experiment the molecules are randomly oriented. Although this is not the proper way to proceed, we may consider as starting point an angular average of the model potential (12), i.e., a central potential

$$U_{i\,\mathrm{mol}}\left(r\right) = \frac{1}{4\pi} \int_{4\pi} d\hat{r}\, V_{i\,\mathrm{mol}}\left(\mathbf{r}\right). \tag{15}$$

This averaging procedure is illustrated through Figure 5.2, where the effective charges $rU_{i\,\mathrm{mol}}\left(r\right)$ and $rV_{i\,\mathrm{mol}}\left(\mathbf{r}\right)$ for two set of angles (θ, ϕ) are compared in the case of CH_4. The effective charge goes from -6 at $r = 0$ and to -1 asymptotically. The minimum is located at $r \approx 2.08$ a.u., i.e. at the equilibrium position of each H atom; its depth and sharpness depend on the orientation and whether the angular average has been performed or not.

The model potential (12) proposed in this work can be certainly improved in many aspects, some of which are under current investigation. One of them is the inclusion of the exchange. Also, as we use an independent particle approximation, some many-body aspects (i.e., correlation) are only included indirectly through the use of MO in Equation (12), but not explicitly.

5.2.2 Driven Equation and Cross Section

To introduce our Sturmian approach, we start with the use of an arbitrary potential $U\left(\mathbf{r}\right)$, such as the one given by Equation (12). We describe the PI process using the first-order perturbation theory for a molecule that interacts with a radiation field. The Hamiltonian can be written as

$$\widehat{\mathcal{H}} = \widehat{H}_0 + \widehat{W}\left(t\right), \tag{16}$$
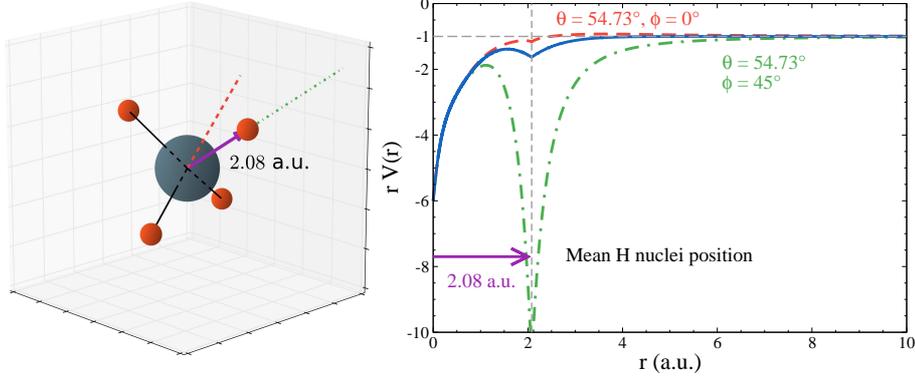
Figure 5.2: (Color online) **Left panel:** Representation of the spatial localization if the individual atoms on CH_4; the mean equilibrium distance is indicated. **Right panel:** Molecular model (12) (red dash and green dash-dot) and angular averaged (15) (blue, solid) potentials for CH_4, at indicated angles. The potential in green (dash-dot) corresponds to the variation of the potential on the the green path on the figure of the left panel.

where $\widehat{H}_0 = \widehat{T} + U\left(\mathbf{r}, \hat{\mathfrak{R}}\right)$ is the field-free Hamiltonian of the target with $\hat{\mathfrak{R}} = (\alpha, \beta, \gamma)$ the set of Euler angles that specify the spatial orientation of the molecule; $\widehat{T}$ is the kinetic energy operator, and

$$\widehat{W}(t) = \begin{cases} -F^{(\mathrm{L})}(t)\,\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{r} = F(t)\,\widehat{D}^{(\mathrm{L})}, & \text{length gauge} \\ -F^{(\mathrm{V})}(t)\,\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} = F(t)\,\widehat{D}^{(\mathrm{V})}, & \text{velocity gauge} \end{cases} \tag{17}$$

where $F^{(\mathrm{g})}(t)$ is the electric field in the length gauge or the vector potential in the velocity gauge, $\hat{\boldsymbol{\varepsilon}}$ gives the polarization of the field and $\widehat{D}$ are the dipolar operators (2); $F(t)$ contains the time-dependent profiles of the radiation field.

Dropping the explicit $\hat{\mathfrak{R}}$-dependence for the moment, we begin with the TDSE for the total Hamiltonian (16)

$$\left(i\frac{\partial}{\partial t} - \widehat{\mathcal{H}}\right)\Psi(\mathbf{r}, t) = \left(i\frac{\partial}{\partial t} - \widehat{H}_0 - \widehat{W}(t)\right)\Psi(\mathbf{r}, t) = 0, \tag{18}$$

and propose the general solution to be

$$\Psi(\mathbf{r}, t) = e^{-i\omega_0 t}\left[\Phi^{(0)}(\mathbf{r}) + \Psi_{\mathrm{scatt}}(\mathbf{r}, t)\right], \tag{19}$$

where $\Phi^{(0)}(\mathbf{r})$ is the wavefunction of the initial ground state of the molecule, usually the active MO to ionize, with energy ω_0, and $\Psi_{\mathrm{scatt}}(\mathbf{r}, t)$ is the wavefunction of the photoelectron, with energy $\omega = E$ (in atomic units). Replacing (19) in (18), we obtain

$$\left[i\frac{\partial}{\partial t} - \omega_0 - \widehat{H}_0 - \widehat{W}(t)\right]\Psi_{\mathrm{scatt}}(\mathbf{r}, t) = \widehat{W}(t)\,\Phi^{(0)}(\mathbf{r}). \tag{20}$$

Now, if we apply a Fourier transform to (20), we obtain the TISE

$$
\left(\omega - \omega_0 - \widehat{H}_0\right) \Psi_{\text{scatt}}\left(\mathbf{r}, \omega\right) - \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega' \widehat{\mathcal{W}}\left(\omega'\right) \Psi_{\text{scatt}}\left(\mathbf{r}, \omega - \omega'\right)
$$
$$
= \widehat{\mathcal{W}}\left(\omega\right) \Phi^{(0)}\left(\mathbf{r}\right),
$$

(21)

where $\widehat{\mathcal{W}}\left(\omega\right)$ is the Fourier transform of $\widehat{W}\left(t\right)$.

Equation (21) contains the interaction with the field to all orders, and therefore $\Psi_{\text{scatt}}\left(\mathbf{r}, \omega\right)$ contains information over all possible processes. Neglecting the integral term of (21), we can introduce a perturbative expansion on the scattering wavefunction [25]. Since we are interested here only in single PI processes, we retain the first order, and then Equation (21) results in the driven equation for the final state wavefunction

$$
\left(\omega - \omega_0 - \widehat{H}_0\right) \Psi^{(1)}\left(\mathbf{r}, \omega\right) = \widehat{\mathcal{W}}\left(\omega\right) \Phi^{(0)}\left(\mathbf{r}\right).
$$

(22)

This is the equation that we want to solve; the scattering wavefunction at first order, $\Psi^{(1)}\left(\mathbf{r}, \omega\right)$, will provide the PI information.

To solve equation (22), we separate first the scattering wavefunction in its radial and angular parts

$$
\Psi^{(1)}\left(\mathbf{r}, \omega\right) = \frac{1}{r} \sum_{\ell m} \varphi_\ell\left(r, \omega\right) Y_\ell^m\left(\hat{r}\right).
$$

(23)

Usually, the radial wavefunction $\varphi_\ell\left(r, \omega\right)$ is expanded in some radial basis set. Within our Sturmian approach it is expanded in a GSF set (see Section 5.1)

$$
\varphi_\ell\left(r, \omega\right) = \sum_j a_j^{(\ell, E)}\left(\omega\right) \mathcal{S}_j^{(\ell, E)}\left(r\right).
$$

(24)

Performing an angular projection, Equation (22) is converted into a set of angular-coupled differential equations

$$
\sum_{\ell m} \left[\left(\omega - \omega_0 + \frac{1}{2}\frac{d^2}{dr^2} - \frac{\ell\left(\ell+1\right)}{2r^2}\right) \delta_{\ell'\ell}\delta_{m'm} - U_{\ell'\ell}^{m'm}\left(r\right)\right] \varphi_\ell\left(r, \omega\right) = \varrho_{\ell'}^{m'}\left(r, \omega\right),
$$

(25)

where $U_{\ell'\ell}^{m'm}\left(r\right) = \langle \ell'm' |U\left(\mathbf{r}\right)| \ell m \rangle$ and $\varrho_{\ell'}^{m'}\left(r, \omega\right) = r \left\langle \ell'm' \left| \widehat{\mathcal{W}}\left(\omega\right) \right| \Phi^{(0)} \right\rangle$. As mentioned in Section 1, the use of a non-central potential to describe the molecular target couples directly the different angular momenta of the initial state. For atoms or angular averaged molecular potentials, on the other hand, there is no coupling, $U_{\ell'\ell}^{m'm}\left(r\right)$ is diagonal and we have a single radial equation

$$
\left(\omega - \omega_0 + \frac{1}{2}\frac{d^2}{dr^2} - \frac{\ell\left(\ell+1\right)}{2r^2} - U\left(r\right)\right) \varphi_\ell\left(r, \omega\right) = \varrho_\ell^m\left(r, \omega\right).
$$

(26)

Recall now that the potential $U\left(\mathbf{r}, \hat{\mathfrak{R}}\right)$ of the field-free Hamiltonian $\widehat{H}_0$ contains the orientation $\hat{\mathfrak{R}}$ of the molecule. This orientation dependence is to be accounted for by $\varphi_\ell\left(r, \omega\right)$ and finally by the coefficients $a_j^{(\ell, E)}\left(\omega\right)$, so that we actually have $a_j^{(\ell, E)}\left(\omega, \hat{\mathfrak{R}}\right)$.

Now, to solve the coupled system of Equations (25), we use the GSF expansion (24), and obtain

$$
\sum_{\ell m} \sum_j \left[\left(\omega - \omega_0 + \frac{1}{2} \frac{d^2}{dr^2} - \frac{\ell (\ell+1)}{2r^2} \right) \delta_{\ell' \ell} \delta_{m'm} - U_{\ell' \ell}^{m'm} (r) \right] \\
\times a_j^{(\ell,\,E)} (\omega)\, \mathcal{S}_j^{(\ell,\,E)} (r) = \varrho_{\ell'}^{m'} (r, \omega) .
\tag{27}
$$

The final step consists in projecting (27) on $\mathcal{S}_i^{(\ell,\,E)} (r)$ (note that it is not the complex conjugate, see Equation (11)): then, all the resulting matrices are calculated as indicated in References 22 and 23. Solving the matricial problem with standard numerical methods provides the coefficients $a_j^{(\ell,\,E)} (\omega)$.

All GSFs of the basis set have the same and correct asymptotic behavior, in this case the behavior dictated by the Coulomb potential (see Section 5.1). This means that our basis functions possess, by construction, important physical information and need to expand essentially the inner region, whose size will be determined by the range of the driven term. This makes the basis set adequate and finally computationally efficient. From the asymptotic property of the GSFs, we obtain the transition amplitude directly from the expansion coefficients of the scattering wavefunction in (24)[267]

$$
\mathcal{T} \left(\omega, \hat{r}, \hat{\mathfrak{R}} \right) = -\sqrt{2\pi} \sum_\ell Y_\ell^m (\hat{r}) \left\langle \Psi_{-\mathbf{k}}^{(-)} \left| \widehat{\mathcal{W}} (\omega) \right| \Phi^{(0)} \right\rangle = \sum_{\ell m j} Y_\ell^m (\hat{r})\, a_j^{(\ell,\,E)} \left(\omega, \hat{\mathfrak{R}} \right) .
\tag{28}
$$

After an angular projection, we finally have the PI cross section as a function of the photon energy[267]

$$
\frac{d\sigma^{(\ell)} \left(\hat{\mathfrak{R}} \right)}{dE} = \frac{4\pi^2 \omega_{ki}^{(\mathrm{g})}}{c}\, k\, \frac{1}{2\pi} \frac{\left| \sum_j a_j^{(\ell,\,E)} \left(\omega, \hat{\mathfrak{R}} \right) \right|^2}{\left| \mathscr{F} (\omega) \right|^2} .
\tag{29}
$$

where $\omega^{(\mathrm{L})} = E - E_0$ or $\omega^{(\mathrm{V})} = (E - E_0)^{-1}$ is the difference between final and initial energies in either length or velocity gauges, and $\mathscr{F} (\omega)$ is the Fourier transform of the radiation field profile $F(t)$.

5.2.3 Example: Hydrogen Atom

The coupled system of equations (27) allows us to study PI processes for any potential. For systems that are described with a central potential, we are left with a single differential equation[267,268]. Applications to a set of different molecules will be given in Section 5.3 and is here illustrated for hydrogen atom. For this atomic target, we solved the TISE (27) in both length and velocity gauges for electron energies in the range $[0.00, 3.00]$. Each one of these energies was used as the fixed energy E to calculate our GSFs basis through (9), where a Coulomb potential with charge -1 was taken as auxiliary potential and a Yukawa potential with an energy-dependent parameter as generating potential. For the initial state we used the exact ground state wavefunction of the atom. Our calculated PI cross section (29) is shown in Figure 5.3, and is compared with the analytical formula given by Harriman[269]. Agreement between the cross sections in both gauges is perfect. Comparing with the analytical formula we obtain errors of the order of $10^{-8} \sim 10^{-11} \%$ over all the energy range (see Figure 5.4), showing that

our results with the selected GSF parameters gives very stable and "numerically exact" solutions to the TISE (22).
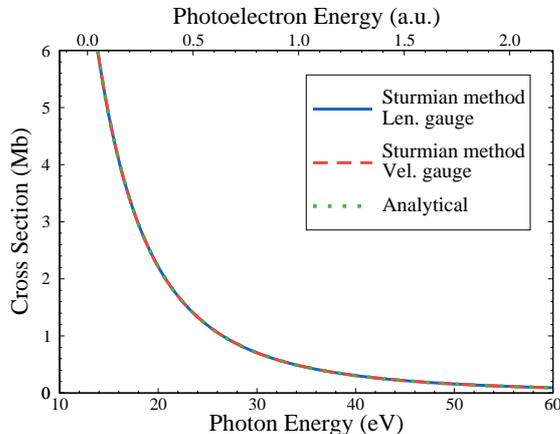
Figure 5.3: (Color online) PI cross section of H atom from the ground state $1s$, in Mb versus photon energy in eV. Our results for length (blue, solid) and velocity (red, dash) and are compared with the exact analytical formula by Harriman[269] (green, dots).
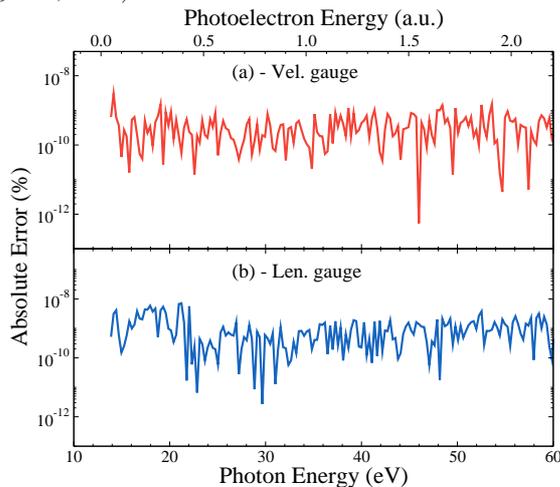
Figure 5.4: (Color online) Absolute errors for the calculated PI cross section in Figure 5.3. **(a):** For the results in velocity gauge and **(b):** in length gauge.

5.3   Results For Molecules

In this section we report some results obtained by applying our Sturmian approach for molecular single PI, first solving Equation (27) for the angular averaged potential (15), and then using the non-central potential (12). Some results have been partially published before[268,270] for CH_4 and H_2O. The treatment of molecular systems with an averaged (central) potential is similar to that of atomic systems. For all cases we used 60 GSFs for each final energy and final

922 (ℓ, m) set; the basis functions are defined in a box of 50 a.u., using an aux-
923 iliary Coulomb potential with charge -1, and a generating Yukawa potential
924 with an energy-dependent parameter. We have verified that in all cases the
925 cross sections are converged in terms of number of GSFs. The initial MO were
926 taken from Moccia publications, specifically for H_2O from Reference [271], for
927 NH_3 from Reference [272] and for CH_4 from [273]. For the non-central potential,
928 with the fixed spatial molecular orientation given by Moccia, we use exactly the
929 same GSF basis and initial MOs. The respective PI cross sections were calcu-
930 lated using Equation (29), and we shall present our results in both length and
931 velocity gauges. It is worth emphasizing here that the majority of theoretical
932 publications on molecular PI present results obtained with the length gauge,
933 but do not provide a detailed analysis of gauge agreement, as it is often done
934 for atomic systems.

5.3.1 H_2O

936 First, we start to study PI from the valence orbitals of H_2O whose electronic
937 ground state configuration is $1a_1^2 \, 2a_1^2 \, 1b_2^2 \, 3a_1^2 \, 1b_1^2 \, {}^1A_1$. We study here only the
938 two valence MOs. For the inner valence orbital $3a_1$ ($E_0 = -15.1323$ eV), the
939 calculated PI cross sections are shown in Figure 5.5, and for the outer orbital
940 $1b_1$ ($E_0 = -13.4805$ eV) in Figure 5.6. Both are compared with TD-DFT
941 calculations by Stener $et\ al$[91], GIPM/D by Kilcoyne $et\ al$[155], STT by Cacelli
942 $et\ al$[199], and ISM by Machado $et\ al$[234]; the experimental data were reported
943 by Banna $et\ al$[274].
944   For the MO $3a_1$, we observe a good agreement between our results in veloc-
945 ity gauge and other theoretical calculations, in particular for photon energies
946 beyond 30 eV, where our results are very close to the TD-DFT and GIPM/D;
947 on the other hand, the length gauge results considerably overestimate the cross
948 sections for all calculated energies. In general, the cross sections for inner va-
949 lence orbitals are difficult to calculate accurately, due to the presence of different
950 many-body effects, as relaxation of the core.
951   For the MO $1b_1$, the gauge discrepancy is of the same order as for the $3a_1$
952 case. Our cross sections compare fairly with other theoretical results, ours being
953 seemingly too low in the threshold region where unfortunately no experimental
954 data are available.
955   The results obtained using the non-central potential (12), are only slightly
956 better, indicating therefore that the central potential (15) is good enough to
957 study this particular molecule.

5.3.2 NH_3

959 Next we study PI for both valence orbitals of NH_3 whose ground state electronic
960 structure is $1a_1^2 \, 2a_1^2 \, 1e^4 \, 3a_1^2 \, {}^1A_1$. For the inner valence MO $1e$ ($E_0 = -16.2071$
961 eV), the cross section is shown in Figure 5.7, and for the outer valence MO $3a_1$
962 ($E_0 = -11.2819$ eV) in Figure 5.8. Our results are compared with the TD-DFT
963 results by Stener $et\ al$[91], GIPM/D by Kilcoyne $et\ al$[155], STT by Cacelli $et\ al$[199],
964 and with calculations using MCF by Nascimento $et\ al$[248]; the experimental data
965 were reported by Brion $et\ al$[275].
966   For the orbital $1e$, our results in velocity gauge show only a fair agreement
967 with all reported data, in particular at high photon energies. Gauge discrepancy
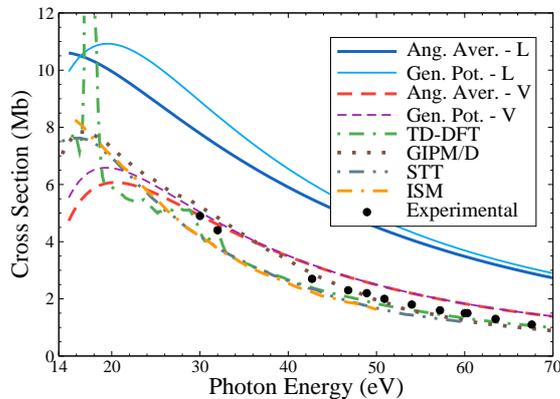
Figure 5.5: (Color online) Partial PI cross section in Mb versus photon energy in eV from the MO $3a_1$ of H_2O. Our results using the angular averaged molecular potential (15) for length (blue, solid) and velocity (red, dash) gauges, and using the non-central potential (12) in length (light blue, thin solid) and velocity (purple, thin dash) gauges are compared with results for TD-DFT[91] (green, dash-dot); GIPM/D[155] (brown, dots); STT[199] (gray, dash-dot-dot); ISM[234] (orange, dash-dash-dot) and with experimental data[274] (black dots).
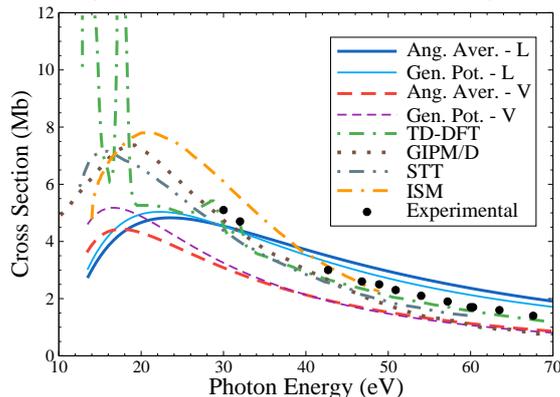
Figure 5.6: (Color online) Same as Figure 5.5 for MO $1b_1$ of H_2O.

is again important and, fortuitously, the length gauge results reproduce the experimental magnitude around 22 eV.

For the orbital $3a_1$, our results exhibit a slightly better gauge agreement; the length gauge cross section presenting the same shape, but with a larger magnitude. The results in velocity gauge are in acceptable agreement with the experimental data over the whole energy range.

As for H_2O, the use of the non-central potential (12) has a small effect, except in length gauge for the $3a_1$ orbital.

5.3.3 CH_4

Finally, we show our results for CH_4 whose ground state electronic structure is $1a_1^2\, 2a_1^2\, 1t_2^6\ {}^1A_1$. The calculated PI cross sections in both length and velocity gauges for the inner valence MO $2a_1$ ($E_0 = -25.0454$ eV) are shown in Fig-
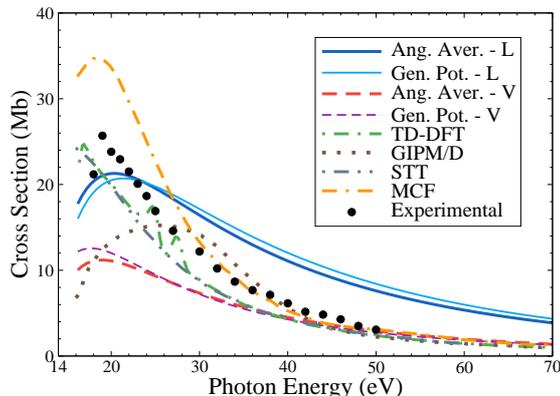
Figure 5.7: (Color online) Partial PI cross section in Mb versus photon energy in eV from the MO $1e$ of NH_3. Our results using the angular averaged potential (15) for length (blue, solid) and velocity (red, dash) gauges, and using the non-central (12) in length (light blue, thin solid) and velocity (purple, thin dash) gauges, are compared with results for TD-DFT[91] (green, dash-dot); GIPM/D[155] (brown, dots); STT[199] (gray, dash-dot-dot); MCF[248] (orange, dash-dash-dot) and with experimental data[275] (black dots).
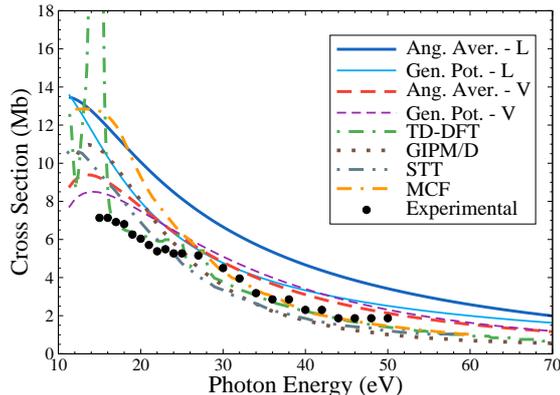
Figure 5.8: (Color online) Same as Figure 5.7 for the MO $3a_1$ of NH_3.

ure 5.9, and for the outer valence MO $1t_2$ ($E_0 = -13.7199$ eV) in Figure 5.10. They are compared with TD-DFT calculations by Stener *et al*[91], GIPM/D by Kilcoyne *et al*[155], MSM by Rosi *et al*[132], and with STT by Cacelli *et al*[200]; the experimental data are taken from Backx and van der Wiel[276].

For the inner valence orbital $2a_1$, the length gauge calculation shows no agreement with any other calculations. For higher energies, say beyond 40 eV, we have a good agreement between our velocity results and experimental and other theoretical data.

For outer valence orbital $1t_2$, results obtained in velocity gauge show a fair agreement with experimental data, at least for photon energies higher than 30 eV; near threshold the position of the experimental peak is rather well reproduced but not its magnitude. Length gauge results are about a factor two too large.
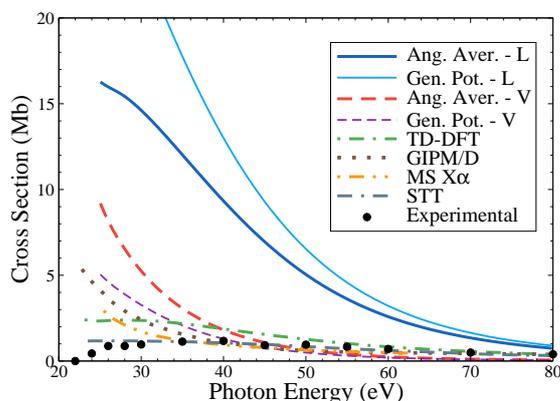
Figure 5.9: (Color online) Partial PI cross section in Mb versus photon energy in eV from the MO $2a_1$ of CH_4. Our results using the central potential (15) for length (blue, solid) and velocity (red, dash) gauges, and using the non-central (12) for length (light blue, thin solid) and velocity (purple, thin dash) gauges, are compared with TD-DFT[91] (green, dash-dot); GIPM/D[155] (brown, dots); MSM[132] (orange, dash-dot-dot); STT[200] (gray, dash-dash-dot) and with experimental data[276] (black dots).
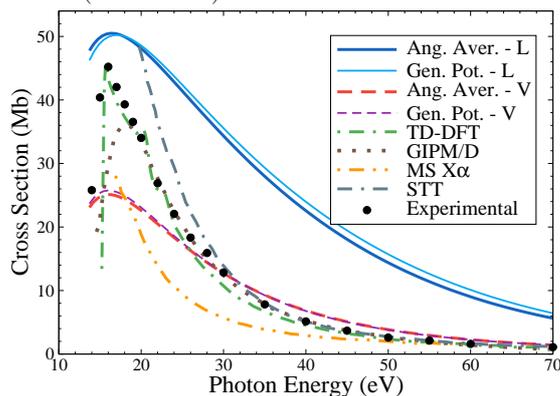
Figure 5.10: (Color online) Same as Figure 5.9 for the MO $1t_2$ of CH_4.

For this molecule, the effect of using the non-central potential (12) is almost unnoticeable for the $1t_2$ orbital but improves the velocity gauge result for the $2a_1$ orbital at lower energies.

As can be observed from Figures 5.5 to 5.10, the Sturmian approach can give reasonable PI cross sections, in particular for ionization from the outer MOs. Some general features are: (i) little difference is seen between the use of the angular averaged (central) potential (15) and the non-central potential (12) (the latter improves marginally the cross sections); (ii) the length gauge results are systematically much larger over the whole energy range than those obtained with the velocity gauge, and are generally not in agreement with other data (experimental or theoretical). This discrepancy indicates that the initial state description needs to be improved; (iii) our velocity gauge results are in overall fair agreement with other theoretical cross sections, in particular for energies

above, say, $15 - 20$ eV over the ionization threshold; (iv) exactly as illustrated in Section 3 with other molecules, the agreement between theoretical results (including ours) and experimental data is not uniform. For energies below 15 eV above ionization threshold agreement is generally poor.

6   Conclusions

In this contribution we explored different theoretical aspects of PI of molecules. The description of this process requires solving quantum mechanically a very difficult many-body and multi-center problem. Contrary to molecular electronic structure calculations, one needs to evaluate a continuum state with appropriate asymptotic conditions. To make calculations feasible, a number of approximations has to be made. Moreover, over the years, a range of theoretical methods and numerical techniques have been proposed. Among them, one finds those familiar in quantum chemistry such as HF, CI and DFT, but also others, such as the RMM, CS or RPA, which encountered great success in atomic scattering calculations and were extended to molecular targets. Since in most experiments the molecules are randomly oriented, an average of the cross sections must be performed over all spatial orientations. This is an extra computational challenge that does not appear when studying collisions with atomic targets.

We began (Section 3) by describing the degree of theoretical-experimental agreement one may find in the literature. The PI of the valence orbitals of H_2, N_2, CO_2 and C_6H_6, are taken as an illustration, and allow to pinpoint some of the challenges one is confronted to. Except for H_2, a non-uniform picture arises. Agreement between theoretical results and experimental data is not always satisfactory; moreover, depending on the molecular orbital which is ionized and the energy range, severe discrepancies are often observed between different calculations. This is due to both the approximations made and the technique adopted. For this reason we provided, in Section 4, a brief description of each method, together with the list of molecules to which they are applied.

We then introduced (Section 5) our Sturmian approach for PI. Essentially, the method provides one-electron basis functions (named Generalized Sturmian Functions) with adequate asymptotic boundary conditions. As they intrinsically contain this property, the basis functions are particularly adequate in describing the ionized electron continuum state. We briefly described how the Sturmian method, developed originally for atoms, may be implemented for molecules with a non-central molecular potential.

As indicated above, in order to reduce the complexity of the problem, different approximations must be considered to make it tractable. In this very first implementation of the Sturmian approach we started with the OCE and the SAE approximations. These reduce considerably the dimension of the problem and allow one to deal with one-electron wavefunctions, an ideal starting point to test the versatility of our method for molecules. It is well known that these approximations are good enough to study symmetric molecules, and in particular the ones with a heavy nucleus in its center of mass; this is the case for the selected molecules in this work (H_2O, NH_3 and CH_4) for which we reported results for PI from their valence orbitals. We stress here that the computational procedure to obtain such results is exactly the same as the one used to study PI in hydrogen atom, with an angular averaged molecular model potential (15).

The same GSF basis and initial state wavefunctions are used for calculations with the non-central potential (12). It turns out that the use of the latter only slightly improves the calculated cross sections. A systematic gauge comparison clearly showed that the length gauge largely overestimates the spectra at all energies. Considering some of the crude approximations, we may state that the implemented technique yields velocity gauge cross sections in reasonable agreement with experimental data, in particular at higher photoelectron energies. Although clearly perfectible (see below), these results are promising since they demonstrate that we have a working computational tool to study the electronic spectra of different molecules.

Let us add a short comment on computational efficiency. As illustrated by several bound-state calculations reported in our review[22] (and references therein), the GSF method is able to deliver results with high accuracy and low computational cost. For scattering calculations, although there is not a rigorous way to perform efficiency comparisons, some estimations were given in Reference 277 with studies of three-body atomic breakup problems. Comparisons between the GSF and state-of-the-art methods proved that our methodology improves the numerical efficiency by at least an order of magnitude. Recently, in a study of DPI of He[278], the GSF method reproduced very precisely ECS differential cross sections with a substantial gain (more than 50%) in memory storage of Hamiltonian matrix. In the present molecular applications the GSF tool is similar. The built in properties make the GSF set very adequate (and, to our mind, efficient) to deal with scattering problems, here PI.

The use of the angular averaged molecular model potential, which is equivalent to include the random orientation of the molecule before the scattering calculations, gave us good results for high energies; for lower energies a better description of the target is clearly necessary. Besides the molecular potential itself, in that regime all the many-body effects are important, and the wavefunction for the initial state should include all active electrons. In that respect, we tried to include exchange terms in different manners. In our preliminary attempts, such terms did not remove the observed gauge discrepancies; we are currently investigating other ways to include in our model both exchange and correlations effects. Furthermore, the interactions with all nuclei becoming important, a many-center wavefunction should be employed; this may lead in a very expensive description of the system from the computational point of view, particularly for polyatomic molecules. The use of a non-central molecular potential (12) gives slightly better results in the low photon energy regime, since it is a more realistic description of the molecule. However, in this case the cross sections must be calculated for any Euler angles set. The final angular average over all possible spatial orientations of the molecule in the laboratory frame (defined by the polarization of the radiation field) is then computationally much more expensive. Moreover, in all investigated systems, in particular for inner valence orbitals, we saw that our length gauge results are always overestimating experimental data. The gauge discrepancies are known (see, for instance, References 89, 199, 200, 202, 268 or 279), but are rarely discussed in the literature for molecular cases. They can be related to the quality of the wavefunctions for the initial state and also by the absence of different many-body effects. In order to obtain a better gauge agreement, one would need to use more sophisticated wave functions and avoid the FC and SAE approximations, since in some cases the relaxation effects are important, as it has been shown by TD-DFT results

(see Sections 3, 4.3.2 and Figures 5.6 and 5.10).

As a summary, we have presented here some results of a first implementation of our Sturmian approach to study PI of molecules. Improvements of calculated cross sections may be obtained using more realistic molecular potentials and initial wavefunctions. Investigations in this direction are under way and will be presented elsewhere. GSFs offer also a promising tool to study other ionization processes in molecular systems such as the single ionization by electron impact, the so-called $(e, 2e)$ process.

Acknowledgments

A   List of Photoionization Calculations for Different Molecules

We list here, molecule by molecule, the references of all applications of theoretical methods mentioned in Section 4.

Homonuclear diatomic

1. H_2^+ [108,109,114,115,118,211,213,254 251–253]

2. H_2 [27,32,33,35,36,57,59,60,75,76 110–112,116,118,121,128,145–147 150,153,154,164,165,167,168,176–178 195,217,236,252]

3. D_2 [27,165]

4. Li_2 [68]

5. C_2 [1]

6. N_2 [38–42,51,67,89,101,121 117,128,129,131,145–149,151 153,154,170,171,174,175,179–181,185 193,217]

7. O_2 [65]

8. F_2 [204]

9. Cl_2 [84]

Heteronuclear diatomic

10. HeH^{2+} [254]

11. HeH^+ [58,169]

12. LiH [183]

13. CH [194]

14. OH [237]

15. HF [77,82,91,148,153,188,200]

16. CN^- [171]

17. CO [34,40,44,51,67,71,92,93,101,102 128,131,146,148–151,171,203,219]

18. NO [121,170]

19. HCl [54,82,201]

Polyatomic

20. BH_3 [82]

21. H_2O [82,91,146,148–151,154,155,171 188,196–199,234,241,268]

22. NH_3 [82,91,149,155,171,188,199,220,248]

23. $LiCN$ [62]

24. AlH_3 [82]

25. H_2S [82,146,149,182,202,241]

26. PH_3 [82,89,149]

27. SiH_4 [82,134,235]

28. CO_2 [41,44–46,53,69,121,131,171,230]

29. NO_2 [41,44,70,171]

30. NO_2^- [171]

31. O_3 [55]

32. C_2N_2 [41,148]

33. $CaHN$ [148]

34. C_2O_2 [84]

35. COS [131]

36. NF_3 [138]

37. CS_2 [49,131]

38. CF_4 [95,96,132,233]

39. PF_3 [135,138]

40. CF_3Cl [137]

41. SiF_4 [134]

42. SF_6 [41,221,232]

43. CCl_4 [233]

44. $SiCl_4$ [133,134]

45. $TiCl_4$ [41]

Organic molecules

46. CH_3 [241]

47. CH_4 [66,82,91,132,145–147,149–151 155,171,188,200,233,238,268,270]

48. CH_3I [136]

49. H_2CO [241]

50. C_2H_2 [39,94,98,151,171,181,184,231,239]

51. C_2H_4 [50,98,130,145,146,150,171]

52. C_2H_6 [171]

53. $C_2(CN)_2$ [148]

54. C_3H_6O (methyl-oxirane) [86]

55. C_3H_8 [171]

56. $(CH_3)_2S$ [149]

57. C_4H_6 [63]

58. C_4H_4O (furan) [148]

59. C_4H_5N (pyrrole) [148]

60. $C_4H_4N_2$ (pyrimidine) [97]

61. $C_4H_4N_2$ (pyrazine) [97]

62. $C_4H_4N_2O_2$ (uracil) [87]

63. C_6H_6 (benzene) [48,50,51,85,205]

64. C_6F_6 [149]

65. $C_4F_4N_2$ [148]

66. $Cr(CO)_6$ [41,84]

67. $C_{10}H_8$ (naphthalene) [85]

68. $C_{14}H_{10}$ (anthracene) [85]

69. $C_{16}H_{10}$ (pyrene) [85]

Fullerenes

70. C_{20} [187]

71. C_{60}^+ [186]

72. C_{60} [99,187,240]

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