



Generalized Sturmian Functions in prolate spheroidal coordinates: Continuum states

Dario Mitnik^a, Ana Laura Frapiccini^b, and Lorenzo Ugo Ancarani^{c,*}

^aInstituto de Astronomía y Física del Espacio (IAFE), CONICET-UBA, C.C. 67, Buenos Aires, Argentina

^bIFISUR, Universidad Nacional del Sur, CONICET, Departamento de Física—UNS, Bahía Blanca, Argentina

^cUniversité de Lorraine, CNRS, Laboratoire de Physique et Chimie Théoriques, Metz, France

*Corresponding author: e-mail address: ugo.ancarani@univ-lorraine.fr

Contents

1. Introduction	239
2. Generalized Sturmian Functions method	242
2.1 Prolate coordinates and the Schrödinger equation	242
2.2 Sturmian approach	244
3. Results	247
3.1 Continuum states	247
3.2 Photoionization cross section	248
4. Summary	251
Acknowledgments	252
References	252

Abstract

We propose and implement a spectral approach to describe continuum states of diatomic systems. The method is based on Generalized Sturmian Functions in prolate spheroidal coordinates. With the one-electron dihydrogen cation as an example, we demonstrate the numerical efficiency by calculating photoionization cross sections.



1. Introduction

The molecular ion H_2^+ is the simplest stable molecular system, and is presented in standard molecular physics books since it allows one to understand why molecules form. Besides, this one-electron molecular ion is involved in many reactions that finally produce polyatomic molecules, and is thus important for example in astrophysics.

H_2^+ (as well as its isotopologues) is composed of two nuclei and an electron, constituting a quantum three-body problem with Coulomb interactions which has been extensively studied since the early days of quantum mechanics.¹⁻³ It was rapidly recognized that prolate spheroidal coordinates, which possess the natural symmetry of diatomic systems, are the best suited choice since they make the Schrödinger equation separable (see also Ref. 4).

In quantum chemistry, one is generally interested in obtaining the bound part of the energy spectrum, that is to say finding the energy levels and the corresponding bound-state wavefunctions. For one-electron diatomic systems, in the fixed-nuclei approximation, the molecular three-body problem reduces to solving a system of two coupled ordinary differential equations (one (quasi)radial and one (quasi)angular); while analytical solutions exist formally,¹⁻³ they involve two expansions that are not particularly tractable giving rise to complicated energy equations. One thus generally resorts to one of the numerical methods available in the literature (see, e.g., 5-8 and references therein). Energies and wavefunctions of the ground and several excited states have been obtained with great precision, in particular for the archetypal H_2^+ ion.

The continuum part of the spectrum is of a different nature, and is useful in different contexts, such as scattering studies. One example is provided by the electron attachment to a neutral molecular system. Another example appears when a charged particle, or a photon, interacts with a molecule, since one possible process is ionization of the target. In that case an electron is ejected from a specific orbital of the molecule, with a positive kinetic energy set by energy conservation; such an electron should then be described by a continuum state. The energy being fixed a priori, the corresponding wavefunction, whose spatial part will oscillate up to infinity, remains to be determined. Appropriate scattering boundary conditions have to be imposed and the accurate description of such non- L^2 wavefunctions is therefore more laborious and computationally more expensive. The study of continuum states for atomic systems has a long history, and most methods were developed in spherical coordinates. Some of them have been adapted or extended to molecular systems, whether in a monocentric or a multicentric approach. Closely related to the present work, one such method is the spectral approach that uses one-electron Generalized Sturmian Functions.⁹ Initially applied to atomic systems (including the notorious three-body correlated system (p^+, e^-, e^-)), the approach has then been extended¹⁰ to deal with molecules in a one-center approach (see Ref. 11

for an application to single photoionization and¹² to ionization by electron impact). More recently, the photodouble ionization of water^{13,14} has been studied with a correlated two-electron continuum built with one-electron Generalized Sturmian Functions. Because of their geometry, diatomic molecules in general and one-electron diatomic molecular systems in particular merit a separate treatment; for the continuum part of the spectrum, a number of numerical schemes have been proposed since the 1970s (see, e.g., 15–21 and references therein). Spherical coordinates are not natural for two-center systems, and the use of prolate spheroidal coordinates should provide, in principle, the most effective framework.⁷

We have recently started to investigate diatomic molecules within a Generalized Sturmian Functions approach extended to prolate spheroidal coordinates. As a first step⁸ we looked at the bound states of the molecular ion H_2^+ (and some other heteronuclear ions, such as HHe^{+2} or HLi^{+3}). It turns out that our method is computationally efficient: small basis sets suffice to obtain rather accurate ground and excited states. Besides, the method proved to be robust over a wide range of internuclear distances R , including in the notoriously difficult atomic limit. Although of a different nature, for completeness, we should mention that Coulomb Sturmian Functions in these spheroidal coordinates have been investigated and applied to a similar study of bound states^{7,22} (see also Ref. 23 for some of the underlying mathematics).

In this work, we wish to tackle the second step, that is to say the continuum part of the spectrum. The spectral approach allows one to treat bound and continuum states in a similar fashion, with Generalized Sturmian Functions of, respectively, negative or positive energy. One of the main advantages is that an appropriate asymptotic behavior can be imposed on all basis elements: inserting the correct physics into the basis makes the expansions converge rapidly. While such spectral method has been explored in spherical and hyperspherical coordinates, exploited successfully in atomic systems, and later extended to molecules treated in a monocentric way, we now wish to focus on diatomic molecules, and thus work with prolate spheroidal coordinates. As a start, we present here one-electron basis functions, postponing the study of correlated systems to a later stage. We implement and illustrate the method by obtaining continuum states of H_2^+ which provides a benchmark for numerical issues. The quality of our wavefunctions is tested through time-independent calculations of photoionization cross sections. A single photon ionizes the molecular target, and the electron is ejected into the continuum with a given energy E . Both the initial bound

state and the continuum state of energy E are described within our Sturmian formalism. The cross sections can be compared with results published in the literature.

The rest of the paper is arranged as follows: In [Section 2](#), we begin with the description of a general one-electron system in prolate spheroidal coordinates and outline the proposed Sturmian method. Details of the numerical scheme are also provided. Results of our calculations are presented in [Section 3](#), where photoionization cross sections of the ground state of H_2^+ are compared with those found in the literature. A short summary is given in [Section 4](#).

Atomic units ($\hbar = m_e = e = 1$) are assumed throughout.



2. Generalized Sturmian Functions method

2.1 Prolate coordinates and the Schrödinger equation

We wish to study a diatomic molecular system consisting of one electron and two nuclei of arbitrary charges Z_1 and Z_2 placed at a fixed distance R along a line defining the z -axis (see [Fig. 1](#)). For further use, we set $a_1 = R(Z_1 - Z_2)$ and $a_2 = R(Z_1 + Z_2)$. It is well known that such systems are best investigated with prolate spheroidal coordinates, defined by

$$\xi \equiv \frac{r_1 + r_2}{R} \quad 1 \leq \xi < \infty \quad (1a)$$

$$\eta \equiv \frac{r_1 - r_2}{R} \quad -1 \leq \eta \leq 1 \quad (1b)$$

$$\phi \equiv \arctan\left(\frac{y}{x}\right) \quad 0 \leq \phi \leq 2\pi. \quad (1c)$$

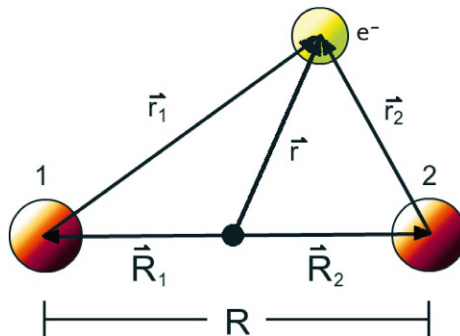


Fig. 1 One-electron diatomic molecule, with two nuclei separated by a distance R , and the electron at a distance r_1 from nucleus 1 and r_2 from nucleus 2.

The volume element is $\frac{R^3}{8}(\xi^2 - \eta^2) d\xi d\eta d\phi$.

The molecular system involves three Coulomb interactions. The electron-nuclei potential is given by

$$V(\xi, \eta) = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2} = -\frac{2}{R^2} \frac{a_2\xi - a_1\eta}{(\xi^2 - \eta^2)}. \quad (2)$$

In the fixed-nuclei approximation, the nuclear repulsive potential energy $1/R$ is an additive constant since the internuclear distance R enters as a parameter.

The Schrödinger equation for the electron (we neglect any nuclei finite mass effect)

$$\left\{ -\frac{2}{R^2(\xi^2 - \eta^2)} \left[\frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial}{\partial \eta} \right] + \frac{\xi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \phi^2} \right\} \psi(\xi, \eta, \phi) = E \psi(\xi, \eta, \phi), \quad (3)$$

is separable in prolate spheroidal coordinates. The solution is expressed as a product of three functions

$$\psi(\xi, \eta, \phi) = U(\xi)\Lambda(\eta)\Phi(\phi). \quad (4)$$

The azimuthal function Φ fulfills the equation

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0, \quad (5)$$

whose solutions are

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad (6)$$

with $m = 0, \pm 1, \pm 2, \pm 3, \dots$ (m is a good quantum number because of the axial symmetry of the potential). Once the azimuthal dependence has been eliminated, we are left with a two variable differential equation

$$\left\{ \frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + a_2\xi \mp p^2\xi^2 - \frac{m^2}{\xi^2 - 1} \right. \\ \left. + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial}{\partial \eta} \right] - a_1\eta \pm p^2\eta^2 - \frac{m^2}{1 - \eta^2} \right\} U(\xi)\Lambda(\eta) = 0, \quad (7)$$

where $p^2 = \frac{|E|R^2}{2} > 0$ is a scaled energy, and the upper sign is for the bound case and the lower sign for continuum states. Eq. (7) is also separable, and one gets a system of two ordinary differential equations

$$\left[\frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + a_2 \xi \mp p^2 \xi^2 - \frac{m^2}{\xi^2 - 1} + A_{mq} \right] U_{mq}(\xi) = 0, \quad (8a)$$

$$\left[\frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial}{\partial \eta} \right] - a_1 \eta \pm p^2 \eta^2 - \frac{m^2}{1 - \eta^2} - A_{mq} \right] \Lambda_{mq}(\eta) = 0, \quad (8b)$$

where the label q refers to the number of zeros of the function $\Lambda_{mq}(\eta)$. The (quasi)radial equation for $U_{mq}(\xi)$ and the (quasi)angular equation for $\Lambda_{mq}(\eta)$, are coupled through both the scaled energy p^2 and the separation constant A_{mq} . States with different m values are not coupled, and can therefore be considered independently.

2.2 Sturmian approach

For both bound and continuum states, we solve the coupled equations using a spectral approach, based on expansions on Sturmian functions in radial and angular coordinates.

2.2.1 Angular

For a given m and q , the solution of Eq. (8b) is proposed as an expansion

$$\Lambda_{|m|,q}(\eta) = \sum_j c_j S_j^a(\eta), \quad (9)$$

on Sturmian functions, i.e., eigenfunctions of the Sturmian equation

$$\left[\frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial}{\partial \eta} \right] - \frac{m^2}{1 - \eta^2} \right] S_j^a(\eta) = -\beta_j S_j^a(\eta), \quad (10)$$

with boundary conditions $S_j^a(1) = 1$ and $S_j^a(-1) = (-1)^j$ for $m = 0$ and $S_j^a(1) = S_j^a(-1) = 0$ for $m \neq 0$. The solutions are actually the well-known associated Legendre polynomials,²⁴ $S_j^a(\eta) = P_j^m(\eta)$, and correspond to eigenvalues $\beta_j = j(j + 1)$.

The normalization of our resulting angular solution $\Lambda_{|m|,q}(\eta)$ is taken such that

$$\int_{-1}^1 \Lambda_{|m|,q}(\eta) \Lambda_{|m|,q'}(\eta) d\eta = \delta_{qq'}. \quad (11)$$

2.2.2 Radial

For the radial part, we propose an expansion

$$U(\xi) = (\xi^2 - 1)^{|m|/2} \sum_j d_j \mathcal{S}_j^r(\xi), \quad (12)$$

on a basis of Generalized Sturmian Functions $\mathcal{S}_j^r(\xi)$ generated by the Sturmian equation

$$\left[\frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + 2\xi |m| \frac{\partial}{\partial \xi} + a_2 \xi - p_s^2 \xi^2 \right] \mathcal{S}_j^r(\xi) = \alpha_j V_s(\xi) \mathcal{S}_j^r(\xi), \quad (13)$$

where α_j are the eigenvalues and $p_s^2 = -\frac{R^2 E_s}{2}$ is a parameter that can be set freely. V_s , known as generating potential, must be a short range potential and we adopt here the same choice as in Ref. 8. The two boundary conditions enforced on the basis are as follows: At $\xi = 1$, we require $\mathcal{S}_j^r(\xi) \neq 0$ and finite (for bound-type Sturmian functions more details are given in Ref. 8). At the other end, for $\xi \rightarrow \infty$, for bound-type functions we simply impose a vanishing $\mathcal{S}_j^r(\xi)$ for large ξ ; technically we fix $\mathcal{S}_j^r(\xi = \xi_{max}) = 0$ where ξ_{max} is the radial box size considered as sufficiently large. For continuum-type Sturmian functions, we impose the sinusoidal behavior (see Eq. 14), still imposing $\mathcal{S}_j^r(\xi = \xi_{max}) = 0$ and normalizing $\mathcal{S}_j^r(\xi)$ so that the last maximum of $\left[\sqrt{\frac{8}{\pi}} \frac{1}{\xi R} \frac{1}{\sqrt{k}} \right]^{-1} \mathcal{S}_j^r(\xi)$ is set to have a unit amplitude.

The choice of E_s is conveniently guided by the physical behavior one wishes to describe, and thus depends on whether one is interested in having a bound or continuum basis.

For a bound state with an a priori unknown energy value, taking $E_s < 0$ close to a guess of the sought after energy turns out to be a good choice. With this choice, all basis elements $\mathcal{S}_j^r(\xi)$ will have an exponential decay $e^{-p_s \xi} = e^{-\sqrt{-E_s R^2/2} \xi}$, and will be suited to build up the radial part of that bound state.

For a continuum state of energy $E = k^2/2 > 0$, taking $E_s = E$ is a natural choice since all basis elements will then intrinsically possess the adequate energy; furthermore, if V_s is taken to be of short range, Eq. (13) indicates that they will all have the correct asymptotic behavior. This is a key feature of our Sturmian approach. Finally, the radial functions $U_{|m|,q}^k(\xi)$ are built to behave asymptotically ($\xi \gg 1$) as^{19,20}

$$U_{|m|,q}^k(\xi) = \sqrt{\frac{8}{\pi}} \frac{1}{\xi R} \frac{1}{\sqrt{k}} \sin \left(\frac{kR\xi}{2} + \frac{Z_1 + Z_2}{k} \ln(kR\xi) - \frac{\ell\pi}{2} + \Delta_{|m|,q} \right), \quad (14)$$

with $\ell = q + |m|$ and $\Delta_{|m|,q}$ a phase, as to be normalized in the energy space

$$\frac{R^3}{8} \int_1^\infty \tilde{U}_{|m|,q}^k(\xi) \tilde{U}_{|m|,q}^{k'}(\xi) \xi^2 d\xi = \delta(E - E'). \quad (15)$$

In both continuum and bound cases, the Sturmian expansions convert the two differential equations into two generalized eigenvalue problems (see details in Ref. 8), solving the eigenvalue problem for the A_{mq} parameters for the angular part and for the eigenvalues p^2 for the radial part. An appropriate choice of E_s will impose the correct energy behavior onto the radial Sturmian functions, ultimately making the basis more efficient from a convergence point of view.

2.2.3 Numerical procedure

For bound states, we adopt an iterative scheme as detailed in Ref. 8 for any given value of the quantum number m . We start from a guess energy value p^2 for a given number q of angular nodes. We solve the angular eigensystem (8b) to find the separation constant A_{mq} . With that value of A_{mq} we then solve the radial eigensystem (8a) with our Sturmian basis and find the energy eigenvalues. We then select the closest eigenvalue to the initial guess and iterate that energy in the angular equation to find the new A_{mq} . The iteration is performed until the energy difference is smaller than 10^{-10} . With just 6 Legendre polynomials to expand the angular part, we found for the ground state an energy of $E_{1\sigma_g} = -1.102634186$ a.u. and $A_{mq} = 0.811729480$.

For continuum states, we proceed as follows: For a given q , we first solve the angular part (8b) for a fixed positive energy E_{mq} ; here again we used 6 Legendre polynomials. For the radial part we then start the search of a ξ_{max} such that at $\xi = \xi_{max}$ that energy eigenvalue E_{mq} has a zero in that endpoint. Starting with a guess value for ξ_{max} around 80 a.u., we perform a bracketing minimum search for the radial (energy) eigenvalue problem, defined as the absolute value of the difference between the searched energy and the closest real eigenvalue. After bracketing we use Brent's method for minimum search,²⁵ up to a tolerance of 10^{-10} .



3. Results

In this paper we consider only the hydrogen molecular ion H_2^+ for which $Z_1 = Z_2 = 1$ and thus $a_1 = 0$. In order to facilitate the comparison with other theoretical results, all calculations were performed for a fixed internuclear distance of $R = 2$ a.u.

3.1 Continuum states

For a given energy E_c , and given numbers m and q , we solve the coupled system of equations. We set ξ_{max} , the maximum of the radial coordinate, close to 80 a.u. The key of the Sturmian method resides in the fact that the asymptotic behavior of the solution is already fulfilled by the basis functions; therefore, only a few elements are needed to expand the internal region. As a numerical check, we have also used B-splines to construct the radial Sturmian basis, and validated all calculations.

As an example, we present in Figs. 2 and 3 the angular and radial solutions we have obtained for $m = 0$, an energy $E_c = 1$ a.u. and for the components $q = 1, 3, 5$. The number of nodes in the angular solutions is clearly observed. To better appreciate the asymptotic radial behavior, we plotted the radial solutions $U_q(\xi)$ multiplied by ξ . This product reaches quite rapidly the asymptotic regime (14); from $\xi = 20$ up to ξ_{max} (not shown) each component $\xi U_q(\xi)$ is essentially a sinus function. For comparison, the ground state is

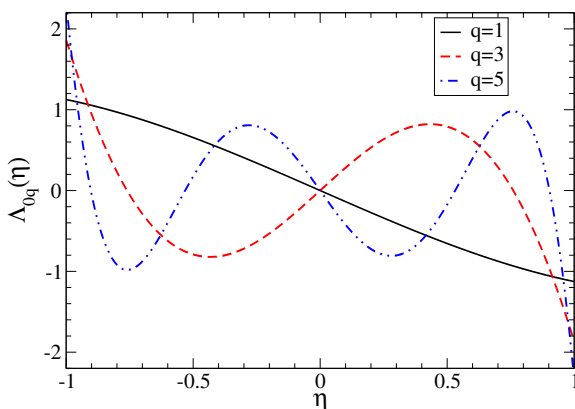


Fig. 2 The angular function $\Lambda_{mq}(\eta)$, solution of Eq. (8b) for $m = 0$ and $q = 1, 3$, and 5 , calculated for $E_c = 1$ a.u. with 6 Legendre polynomials.

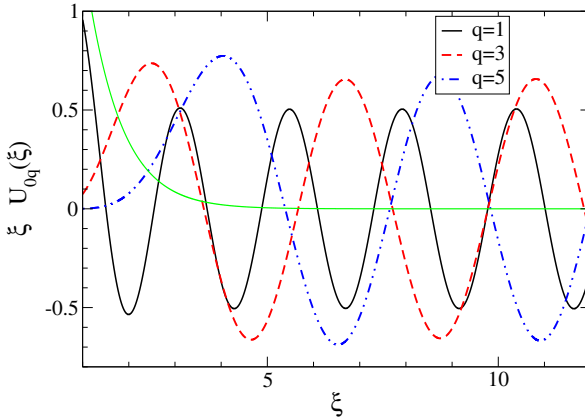


Fig. 3 The radial function $\xi U_{0q}(\xi)$, solution of Eq. (8a) for $m = 0$ and $q = 1, 3$, and 5 , calculated for $E_c = 1$ a.u. with 10 radial Sturmian functions. The radial part of the ground state $\Psi_{1\sigma_g}$ is also plotted (in green).

also included in the figure; the radial function decays very rapidly, being negligible for ξ larger than 10 a.u.

3.2 Photoionization cross section

In order to test the quality of our continuum states, we apply them to study the photoionization of H_2^+ by a single photon of energy ω , and linearly polarized along the \hat{c} direction (here chosen along the z -axis). If the photoelectron is ejected with energy $E_c = k^2/2$, the energy conservation reads

$$\omega = E_c + IP, \quad (16)$$

where IP stands for the ionization potential. Hereafter we assume the molecular target, described by the wavefunction Ψ_i , to be in its ground state $1\sigma_g$ for which $IP = 1.102634$ a.u. Also, we take the continuum state, described by a wavefunction Ψ_k , to be normalized in energy space.

In the dipole approximation, the cross section in the length gauge is given by²⁶

$$\sigma = 4\pi^2\alpha\omega |\langle \Psi_k | \hat{c} \cdot \mathbf{r} | \Psi_i \rangle|^2, \quad (17)$$

where α stands for the fine structure constant. The polarization being along the z -axis, the dipole operator reads $\hat{c} \cdot \mathbf{r} = z = \frac{\xi\eta R}{2}$. In the velocity gauge the definition is given by

$$\sigma = \frac{4\pi^2\alpha}{\omega} |\langle \Psi_k | \hat{\epsilon} \cdot \nabla_{\mathbf{r}} | \Psi_i \rangle|^2, \quad (18)$$

where, for the chosen polarization, the operator reduces to

$$\hat{\epsilon} \cdot \nabla_{\mathbf{r}} = \frac{d}{dz} = \frac{2}{R(\xi^2 - \eta^2)} \left[\eta(\xi^2 - 1) \frac{d}{d\xi} + \xi(1 - \eta^2) \frac{d}{d\eta} \right]. \quad (19)$$

In both cases, the matrix element is a three-dimensional integral over the electronic coordinates. The cross sections calculated in both gauges are equal if exact wavefunctions are used in the matrix element evaluation. Any deviation is a signature of the approximate description of the states involved. Generally speaking, the photoionization process provides an indirect tool to test the theoretical description of the target before and after the interaction, and thus our capacity of describing correlation and many-body effects for both bound and unbound electronic states. In the case of the one-electron ion H_2^+ , there is no correlation, but the present photoionization study provides a stringent test of the final continuum state on which this paper is focused.

Since the ground state $1\sigma_g$ corresponds to $m = 0$, the continuum state will also have $m = 0$. Moreover, the ground state has no zeros ($q = 0$) so that only odd values of q of the continuum will contribute (it turns out that values higher than $q = 5$ do not contribute significantly).

We have calculated, in both the length and velocity formulation, the contribution of different q values, and denote σ_q the corresponding partial cross section. We denote by $\sigma_{total} = \sum_q \sigma_q$. In Table 1 we provide $(1/3)\sigma_q$ for different energies and compare with results from the literature.

From these results, we can make the following statements. Our approach provides very satisfactory results with rather small basis sets. They can be compared, for example, with the 20 angular times 80 radial B-splines with order 7, employed in the calculations presented in Ref. 21. Gauge agreement is also pretty well observed, except for $q = 5$ whose contribution is though rather small relatively to the $q = 1$ and $q = 3$ components.

In Fig. 4 we show the contributions σ_{total} obtained in both length and velocity gauge. We compare our results with those of Bian²¹ obtained with an imaginary-time-propagation (ITP) method (note that Bian gives only length gauge data); the length and velocity gauge results of Tao et al.¹⁸ obtained with the complex scaling method are visually indistinguishable from those of Bian and are not reproduced here. Our results are in very nice agreement over the whole energy range.

Table 1 Partial cross sections $(1/3)\sigma_q$ for the photoionization of the ground state H_2^+ $1\sigma_g \rightarrow E_c\sigma_u$ calculated at a internuclear distance $R = 2$ a.u.

Photoelectron energy $E_c = k^2/2$ (a.u.)	Gauge and source	$E_c p \sigma_u$ $\sigma_{q=1}$ ($\times 10^{-2}$ Mb)	$E_c f \sigma_u$ $\sigma_{q=3}$ ($\times 10^{-2}$ Mb)	$E_c h \sigma_u$ $\sigma_{q=5}$ ($\times 10^{-2}$ Mb)
1	L [present]	0.694	0.933	0.00031
	V [present]	0.698	0.906	0.00071
	L&V ¹⁵	0.694	0.904	0.00042
	L ²¹	0.688	0.907	
2	L [present]	0.516	0.630	0.00632
	V [present]	0.516	0.613	0.00176
	L&V ¹⁵	0.516	0.618	0.00132
	L ²¹	0.517	0.618	
4	L [present]	0.198	0.222	0.00916
	V [present]	0.198	0.218	0.00347
	L&V ¹⁵	0.200	0.222	0.00314
	L ²¹	0.202	0.220	

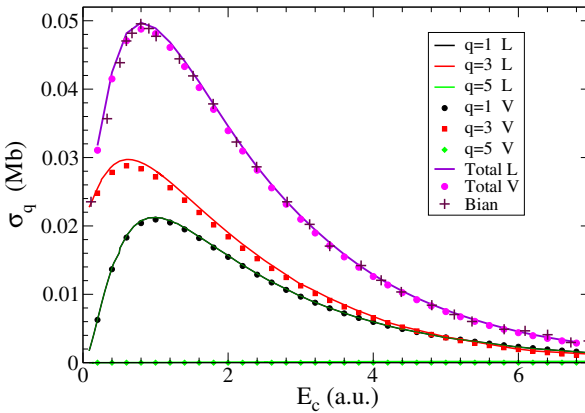


Fig. 4 Cross sections for the photoionization of the ground state of H_2^+ as a function of the photoelectron energy $E_c = k^2/2$.

In Fig. 5 we show the relative contributions σ_q/σ_{total} for $q = 1, 3,$ and 5 . We observe the same trend as featured by the results of Bian.²¹ The total cross section is strongly dominated by the $q = 1$ channel at low energies but this contribution decreases rapidly as the energy increases. At about

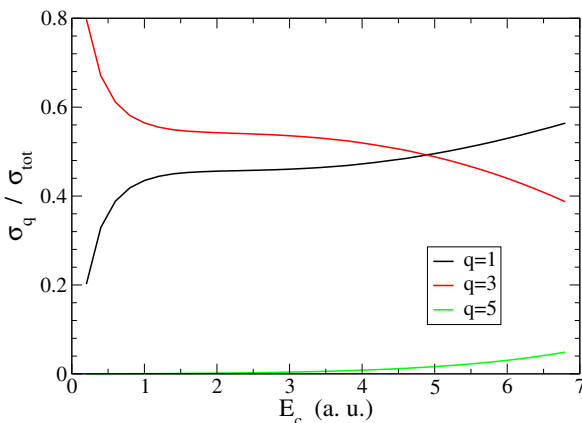


Fig. 5 Relative contribution of each σ_q/σ_{total} (calculated in the length gauge) for the photoionization of the ground state of H_2^+ , as a function of the photoelectron energy $E_c = k^2/2$.

$E_c = 5$ a.u. the $q = 3$ becomes the largest contribution. The $q = 5$ component remains weak throughout the considered energy range (about two orders of magnitude smaller).



4. Summary

We have investigated continuum states of the molecular ion H_2^+ , using expansions on Generalized Sturmian Functions in spheroidal prolate coordinates. The numerical scheme, based on a double expansion in (quasi)radial and (quasi)angular coordinates, is presented and tested. The continuum wavefunction is used to calculate photoionization cross sections which compare very well with data found in the literature. It is worth emphasizing that in our calculation both the initial bound and final continuum states are treated within the same Sturmian approach which proves to be robust, and numerically efficient since only rather small basis are needed. This is due to (i) the use of natural coordinates for this molecular geometry; (ii) the intrinsically physical behavior imposed asymptotically onto the radial Sturmian functions. In line with what was presented in Ref. 8, we are currently also implementing a two-dimensional approach whereby a two-dimensional Sturmian basis set is used.

The present work provides us with positive energy one-electron basis functions suited for diatomic molecules. In a near future, we plan to apply the developed tool to explore angular distributions for the photoionization of one-electron diatomic molecules,^{18,20,27} and study also electron scattering.²⁰

In a more remote future, the idea is to deal with the more challenging two-electron correlated case, by investigating single and double ionization processes on H_2 and on quasi two-electron targets like N_2 .²⁸ Similarly to what was proposed with Generalized Sturmian Functions for atomic systems,²⁹ one way to take up this challenge for many-electrons diatomic molecules is to proceed by constructing correlated functions, with angularly coupled products of the present one-electron Sturmian functions in prolate spheroidal coordinates. Among the two-electron matrix elements, integrals involving the electron-electron interaction $1/|\mathbf{r}_1 - \mathbf{r}_2|$ will be the most difficult to evaluate. However we should be able to make good use of its expansion in prolate spheroidal coordinates, which is given in terms of regular Legendre functions in the angular variables η_1 and η_2 , and the regular and irregular Legendre functions in the radial variables ξ_1 and ξ_2 .³⁰

Acknowledgments

D.M.M. wishes to acknowledge financial support from Agencia Nacional de Promoción Científica y Tecnológica (PICT-2017-2945), Consejo Nacional de Investigaciones Científicas y Técnicas (PIP 11220130100607CO) and Universidad de Buenos Aires (UBACyT 20020170100727BA).

References

1. Burrau, Ø. Berechnung des Energiewertes des Wasserstoff-molekül-ions (H_2^+) im Normalzustand. *Kgl. Danske, Videnskab. Selskab. Mat. Fys. Medd.* **1927**, 7, 14.
2. Hylleraas, E. A. Über die Elektronenterme des Wasserstoffmoleküls. *Z. Phys.* **1931**, 71, 739–763.
3. Jaffé, G. Zur Theorie des Wasserstoffmoleküls. *Z. Phys.* **1934**, 87, 535–544.
4. Komarov, I. V.; Ponomarev, L. I.; Slavyanov, S. Y. *Spheroidal and Coulomb Spheroidal Functions*; Nauka: Moscow, 1976.
5. Carrington, A.; McNab, I.; Montgomerie, C. Spectroscopy of the Hydrogen Molecular Ion. *J. Phys. B: At. Mol. Opt. Phys.* **1989**, 22, 3551–3586.
6. Turbinder, A. V.; Olivares-Pilón, H. The H_2^+ Molecular Ion: A Solution. *J. Phys. B: At. Mol. Opt. Phys.* **2011**, 44, 101002(1–7).
7. Kereselidze, T.; Chkadua, G.; Defrance, P. Coulomb Sturmians in Spheroidal Coordinates and Their Application for Diatomic Molecular Calculations. *Mol. Phys.* **2015**, 113 (22), 3471–3479.
8. Mitnik, D. M.; López, F. A.; Ancarani, L. U. Generalized Sturmian Functions in Prolate Spheroidal Coordinates. *Mol. Phys.* **2021**, e1881179(1–17).
9. Gasaneo, G.; Ancarani, L. U.; Mitnik, D. M.; Randazzo, J. M.; Frapiccini, A. L.; Colavecchia, F. D. Three-Body Coulomb Problems With Generalized Sturmian Functions. *Adv. Quantum Chem.* **2013**, 67, 153–216.
10. Granados Castro, C. M. Application of Generalized Sturmian Basis Functions to Molecular Systems. Ph.D. Thesis, Université de Lorraine, France and Universidad Nacional del Sur, Argentina 2016.
11. Granados-Castro, C. M.; Ancarani, L. U.; Gasaneo, G.; Mitnik, D. M. A Sturmian Approach to Photoionization of Molecules. *Adv. Quantum Chem.* **2016**, 73, 3–57.

12. Granados-Castro, C. M.; Ancarani, L. U. Electron Impact Ionization of the Outer Valence Orbital $1t_2$ of CH_4 . *Eur. Phys. J. D* **2017**, *71*, 65(1-10).
13. Randazzo, J. M.; Turri, G.; Bolognesi, P.; Mathis, J.; Ancarani, L. U.; Avaldi, L. Photo-Double-Ionization of Water at 20 eV Above Threshold. *Phys. Rev. A* **2020**, *101*, 033407(1-9).
14. Bolognesi, P.; Randazzo, J. M.; Turri, G.; Mathis, J.; Penson, C.; Ancarani, L. U.; Avaldi, L. A Combined Experimental and Theoretical Study of Photodouble Ionization of Water at 32 eV Excess Energy and Unequal Energy Sharing. *J. Phys. B: At. Mol. Opt. Phys.* **2021**, *54*, 034002(1-9).
15. Richards, J. A.; Larkins, F. P. Photoionisation Cross Section Calculations of H_2 and H_2^+ Using Numerical Continuum Wavefunctions. *J. Phys. B: At. Mol. Phys.* **1986**, *19*, 1945-1957.
16. Tergiman, Y. S. Continuum Radial Wavefunctions for the One-Electron State of the Coulomb Two-Centre Problem: Characteristic Exponent and Hill Determinant. *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29*, 1035-1044.
17. Rescigno, T. N.; Horner, D. A.; Yip, F. L.; McCurdy, C. W. Hybrid Approach to Molecular Continuum Processes Combining Gaussian Basis Functions and the Discrete Variable Representation. *Phys. Rev. A* **2005**, *72*, 052709(1-8).
18. Tao, L.; McCurdy, C. W.; Rescigno, T. N. Grid-Based Methods for Diatomic Quantum Scattering Problems: A Finite-Element Discrete-Variable Representation in Prolate Spheroidal Coordinates. *Phys. Rev. A* **2009**, *79*, 012719(1-9).
19. Guan, X.; Secor, E. B.; Bartschat, K.; Schneider, B. I. Multiphoton Ionization of H_2^+ in xuv Laser Pulses. *Phys. Rev. A* **2011**, *84*, 033420(1-13).
20. Miyagi, H.; Morishita, T.; Watanabe, S. Electron Scattering and Photoionization of One-Electron Diatomic Molecules. *Phys. Rev. A* **2012**, *85*, 022708(1-11).
21. Bian, X. B. Photoionization of Atoms and Molecules Studied by the Crank-Nicolson Method. *Phys. Rev. A* **2014**, *90*, 033403(1-9).
22. Kereselidze, T.; Chkadua, G.; Defrance, P.; Ogilvie, J. F. Derivation, Properties and Application of Coulomb Sturmians Defined in Spheroidal Coordinates. *Mol. Phys.* **2015**, *114* (1), 148-161.
23. Coletti, C.; Calderini, D.; Aquilanti, V. D-Dimensional Kepler-Coulomb Sturmians and Hyperspherical Harmonics as Complete Orthonormal Atomic and Molecular Orbitals. *Adv. Quantum Chem.* **2013**, *67*, 73-127.
24. Edmonds, A. R. *Angular Momentum in Quantum Mechanics*; Princeton University Press: Princeton, NJ, 1957.
25. William, H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes: The Art of Scientific Computing*, 3rd ed.; Cambridge University Press: NY, 2007.
26. Bransden, B. H.; Joachain, C. J. *The Physics of Atoms and Molecules*; Longman Scientific and Technical: Harlow, UK, 1983.
27. Foster, M.; Colgan, J.; Al-Hagan, O.; Peacher, J. L.; Madison, D. H.; Pindzola, M. S. Angular Distributions From Photoionization of H_2^+ . *Phys. Rev. A* **2007**, *75*, 062707(1-5).
28. Bulychov, A. A.; Chuluunbaatar, O.; Gusev, A. A.; Joulakian, B. (γ , 2e) Photo-Double Ionization of N_2 Molecules for Equal Energy Sharing. *J. Phys. B: At. Mol. Opt. Phys.* **2013**, *46*, 185203(1-9).
29. Randazzo, J. M.; Mitnik, D.; Gasaneo, G.; Ancarani, L. U.; Colavecchia, F. D. Double Photoionization of Helium: A Generalized Sturmian Approach. *Eur. Phys. J. D* **2015**, *69*, 189(1-10).
30. Morse, P. M.; Feshbach, H. *Methods of Theoretical Physics Parts I and II*; McGraw-Hill: New York, 1953.