Hydrogenoid orbitals revisited: From Slater orbitals to Coulomb Sturmians[#]

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Abstract.   The simple connection between the Slater orbitals, venerable in quantum chemistry, and the Coulomb Sturmian orbitals, more recently employed in atomic and molecular physics, is pointed out explicitly in view of the renewed interest in both as basis sets in applied quantum mechanics. Research in Slater orbitals mainly concerns multicentre, many-body integrals, whereas that on Sturmians exploits their orthonormality and completeness with no need of continuum states. An account of recent progress is outlined, also with reference to relationships between the two basis sets, and with the momentum space and hyperspherical harmonics representations.

Keywords.   Sturmians; hyperspherical harmonics; Slater orbitals.

1.   Introduction

Traditionally, in quantum chemistry problems, the search for wavefunctions, i.e., the solutions of the Schrödinger equation for a given complex system, is a demanding challenge involving the mathematical analysis of differential equations; the main route is their expansion as linear combinations of known functions, the 'basis set'. Thanks to the growth of computing memory and speed, the research in these basis set functions continues, allowing calculations of increasing accuracy. Initially, hydrogen-like and Slater-type orbitals were used as convenient basis sets: the former because they are the solution to the Schrödinger equation for a physically defined problem as that of the hydrogen atom, the latter because the introduction of empirical parameters simplifies the overall machinery by accelerating convergence. These two classes of functions were studied for a long time, until the majority of the scientific community preferred to use instead Gaussian-type functions, since they turned out easier for actual, even large scale, calculations.

In parallel, the Sturmian-type orbitals were introduced owing to their capacity of representing the true wavefunction's behaviour (cusps and decay at great interparticle distances) and of producing an infinite and discrete eigenvalue spectrum, complete without adding continuum state. In the Website of http://sturmian. kvante.org, where John Avery and James Avery highlight the on-going activity on Sturmians. Even if the algorithms based on Gaussian-type orbitals are amply implemented in available programs, the Sturmian-type orbitals are currently used in atomic and molecular physics[1] (reference 1 and therein). However, more recent developments of algorithms based on Slater-type orbitals[2] open new paths for applications of exponential-type orbitals.

Definitions of the basis sets are provided in section 2. The main objective of this article is to discuss the relationships between Slater orbitals and Sturmians, permitting to jointly exploit the properties of both (section 3). In section 4, we briefly sketch the advances from the use of momentum space representation, which exploits the Fock projection to analyse the hidden symmetries and therefore bringing in important conceptual and analytical tools involving powerful group theoretical ideas.

2.   Hydrogenoid orbitals and their variants

Historically, most of the mathematical equations of dynamics and mechanics are written in configuration space, where each object of the system is associated to coordinates that specify its position with respect to the origin of the reference frame fixed in space or

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relatively to each other. This is the standard approach of classical mechanics for the motion of planets or projectiles, because we are interested in the position of these objects. In the same way, the time-independent Schrödinger equation for the hydrogen atom:

$$\hat{H}\varphi = E\varphi, \tag{1}$$

where the Hamiltonian $\hat{H} = \hat{T} + V$ is in atomic units, involves a Coulomb potential

$$\hat{H} = \left[-\frac{1}{2}\nabla^2 - \frac{1}{r} \right], \tag{2}$$

where ∇^2 is a three-dimensional Laplacian and r is the distance between the electron and the nucleus.

The exact solution of Equation (1), denoted as hydrogenoid orbitals,[3] is presented in the following explicit notation:

$$\varphi_{nlm}^{\alpha} = N_{nl}^{\alpha}(2\alpha r)^l e^{-\alpha r} L_{n-l-1}^{2l+1}(2\alpha r)Y_{lm}(\hat{r}) \tag{3}$$

where L_{n-l-1}^{2l+1} is a Laguerre polynomial and

$$Y_{lm}(\hat{r}) = \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!} \right]^{\frac{1}{2}} \frac{i^{m+|m|}}{2^l l!}(1-\cos^2\vartheta)^{\frac{|m|}{2}}$$

$$\times \left(\frac{d}{d\cos\vartheta} \right)^{l+|m|} (\cos^2\vartheta - 1)e^{im\varphi} \tag{4}$$

is a spherical harmonic, with $\hat{r}$ indicating collectively the polar angles ϑ and φ. The normalization constant N_{nl}^{α} is given by

$$N_{nl}^{\alpha} = 2\left[\frac{(\frac{\alpha^3}{n})(n-l-1)!}{(n+l)!} \right]^{\frac{1}{2}} \quad \text{with} \quad \alpha = Z/n,$$

where Z and n are the charge of the nucleus and the principal quantum number, respectively. Hydrogenoid orbitals span an orthonormal basis set of the Hilbert space that contains the non-analytic solutions for other problems from many-electron atoms to molecules. In quantum chemistry calculations, the unknown wavefunction of a given atomic or molecular system can be written as linear combination of the hydrogenoid orbitals and next the expansion coefficients are calculated solving a linear algebra problem by applying diagonalization techniques. Poor performances of this apparently straightforward procedure suggested more rigorous approaches (via the Sturmian basis sets on section 2.1) or empirically adjusted alternatives (via Slater type orbitals, see section 2.2). The connection between them is established in the next section 3.

2.1 Sturmian orbitals

The above introduced hydrogenoid orbitals, when used as basis sets, possess several advantages but also drawbacks. The Schrödinger equation represents all the states (either bound or unbound) of an atom. The experiments show that a ionized gas of H atom has a continuum emission spectrum but, at the same time, when we have bound states, the absorption spectroscopy leads to a discrete spectrum. Accordingly, the eigenvalues, that represent the energies of the hydrogen atom, have to agree with the experimental results. If we solve the equation for negative values of the energy, we obtain discrete eigenvalues and normalizable eigenfunctions; conversely, when we use positive energy the spectrum of the eigenvalues becomes continuous and the eigenfunctions are no more normalizable. Thus, if we want to use a complete basis set to describe an unknown wavefunction, Ψ, using hydrogenoid orbitals, we have to use the expansion in eigenfunctions φ_n and φ_N of the two parts of the spectrum, the discrete and the continuum one, and the equation becomes:

$$\Psi = \sum_n c_n\varphi_n + \int c_N\varphi_N dN, \tag{5}$$

where n identifies the first part of the spectrum and the variable N spans the continuum.

Continuum basis sets imply inextricable mathematical problems in the consequent steps. In 1962 Rotenberg[4,5] introduced Sturmian orbitals,[6] as the solution of the differential equation when looking for a complete basis set which does not include the continuum,

$$(\hat{T} + E_0)\psi = \frac{\alpha_{nl}}{r}\psi, \tag{6}$$

where E_0 is a fixed negative value of energy and $\alpha_{nl} = np_0$ is the eigenvalue of the charge, which is varied until the boundary condition are satisfied. Equation 6 belongs to the class of Sturm-Liouville differential equations, which has an infinite set of discrete eigenvalues, strictly increasing. A variable charge does not mean that the electronic charge is no more a universal constant: simply, the charge univocally determines the corresponding eigenfunction. The Sturmian orbitals, fully denoted ψ_{nlm},[7] are the solutions of equation 6 here written as follows:

$$\psi_{nlm}(r) = N_{nl}(2p_0 r)^l e^{-p_0 r}$$

$$\times F(l+1-n \mid 2l+2 \mid 2p_0 r)Y_{ml}(\hat{r}) \tag{7}$$

with $N_{nl} = \frac{2p_0^{\frac{3}{2}}}{(2l+1)!}\left[\frac{(l+m)!}{2n(n-l-1)}\right]$ and $F(l + 1 - n|2l + 2|2p_0r)$ is the confluent hypergeometric function.[8] Sturmian orbitals possess an interesting orthonormal property that can be easily demonstrated. Let us have two distinct eigenfunctions of our basis set which are solutions of the following equations:

$$\left[-\frac{1}{2}\nabla^2 + E_0 - \frac{np_0}{r}\right]\psi_{nlm} = 0 \qquad (8)$$

and

$$\left[-\frac{1}{2}\nabla^2 + E_0 - \frac{n'p_0}{r}\right]\psi_{n'l'm'} = 0. \qquad (9)$$

If we multiply each equation by complex conjugate function ψ_{nlm}^* and $\psi_{n'l'm'}^*$, and integrate over all space, subtracting equation 9 from 8, thanks to the orthonormal property of spherical harmonics inside Sturmian (see Equation 3) and the Virial theorem, we can write:

$$\int \psi_{n'l'm'}^* \frac{1}{r}\psi_{nlm}d^3x = \frac{p_0}{n}\delta_{n'n}\delta_{l'l}\delta_{m'm}. \qquad (10)$$

As can be seen, this equation represents the condition of orthonormality scaled on the potential. A convenient alternative, not requiring complex conjugation, is described in reference 1.

2.2 Slater orbitals

In 1930, Slater[9] introduced a new class of orbitals called by his name; it was created empirically by fitting the experimental data from atomic spectra. The largest difference between Slater-type and hydrogenoid or Sturmians orbitals is the absence of nodes in the radial dependence of the wavefunction. As can be seen by the explicit expression

$$\chi_{nlm}^\zeta = N_n^\zeta r^{n-1}e^{-\zeta r}Y_{lm}(\hat{r}), \qquad (11)$$

there is no polynomial dependence on the principal and the angular momentum quantum numbers, n and l, respectively. In equation 11, the effective charge, ζ, operating on the electron is an adjustable parameter which best reproduces experimental data; $N_n^\zeta = \frac{(2\zeta)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}}$ is the normalization factor. Slater-type orbitals obey the following orthonormality rule

$$\int \chi_{nlm}^* \chi_{n'l'm'}dr = \delta_{ll'}\delta_{mm'}\frac{(n+n')!}{(\zeta + \zeta')^{n+n'+1}}. \qquad (12)$$

3. Relationship between Sturmian and Slater orbitals

Since both types of orbitals are used as an expansion basis set to approximate the true wavefunction of the system, we can assume that there is interest in the possibility of finding the exact relationship between them. Hence, we look for an expansion of a given hydrogenoid orbital φ_{nlm}^α as a linear combination of Slater-type orbital[3]

$$\varphi_{nlm}^\alpha(r) = \sum_{k=0}^{n-l-1}\alpha_k^{nl}\chi_{vlm}^\zeta(r), \qquad (13)$$

where

$$\alpha_k^{nl} = \frac{N_{nl}^\alpha}{N_v^\zeta}\frac{(n+l)!}{(n-l-1)!(2l+1)!}\frac{(-n+l+1)_k}{(2l+2)_k}\frac{(2\zeta)^{k+l}}{k!}, \qquad (14)$$

where $v = k+l+1$ and α_k^{nl} represents a numerical coefficient to be determined. From equation 7 we note that Sturmian orbitals are very similar to the hydrogenoid ones, by writing the Laguerre polynomials $L_{n-l-1}^{2l+1}(2\alpha r)$ as a confluent hypergeometric function:[8]

$$L_{n-l-1}^{2l+1}(2\alpha r) = \left[\frac{(n+l)!}{(n-l-1)!(2l+1)!}\right] \times F(-n+l+1|2l+2|2\alpha r). \qquad (15)$$

Now we are able to rewrite the relation between Sturmian and hydrogenoid orbitals by using a change of variable[3]

$$\psi_{nlm}(r) = \alpha_{nl}^{\frac{3}{2}}\varphi_{nlm}(\alpha_{nl}r) \qquad (16)$$

with $\alpha_{nl} = \frac{n(-2E_0)^{\frac{1}{2}}}{Z}$. If we replace Equation 15 in the Sturmian-type orbitals (7), we directly obtain the relationship as given in Equation 16:

$$\psi_{nlm}(r) = 2p_0^{\frac{3}{2}}\sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \times (2p_0r)^l e^{-p_0r}L_{n-l-1}^{2l+1}(2p_0r)Y_{lm}(\hat{r}). \qquad (17)$$

If we want to write Sturmian orbitals using Laguerre polynomials, it is necessary to pay attention to the different notations in mathematical and quantum chemistry papers. We define the generalized Laguerre polynomial according to the following summation:

$$L_n^a(x) = \sum_{k=0}^{n}(-1)^k\binom{n+a}{n-k}\frac{x^k}{k!}, \qquad (18)$$

but we have to multiply by a factor $1/(n+a)!$[10] to agree with the usual notations.

If we want to close the circle, looking for the relationship between Sturmian and Slater-type orbital, it is natural to search for the expression as a linear combination. In table 1, we show the relation between the first orbitals of the two families:[6] it was obtained by direct comparison of the explicit expressions. The coefficients of the linear combinations are very simple because they were written for the specific case of H_2^+, where p_0 and ζ have the same value. If the energy is fixed at $E_0 = \frac{1}{2}$ in Equation 6 we obtain $p_0 = 1$, i.e., the hydrogenoid orbitals. At the same time, if there is just one shielding electron the effective charge is $\zeta = 1$.

To find the general relationship it is necessary to multiply the variable of the Slater orbital by a coefficient $\beta = \frac{p_0}{\zeta}$, rewriting the defining equation as follows

$$\tilde{\chi}_{nlm}(\beta r) = N_n^\zeta (2p_0 r)^{n-1} e^{-p_0 r} Y_{lm}(\hat{r}) \quad (19)$$

with

$$N_n^\zeta = \frac{\beta^{n+\frac{1}{2}}}{2p_o^{n-1}} \frac{(2\zeta)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}}.$$

We omit $e^{-p_0 r} Y_{lm}$ because it is present in both equations (7) and (19). If we multiply eq. 19 by the coefficient $\frac{N_{nl}^{p_0}}{N_n^\zeta}$ it is possible to obtain a monomial that we replace inside the Sturmian equation

$$\psi_{nlm}(r) = (2p_0 r)^l L_{n-l-1}^{2l+1}(\tilde{\chi}_{vlm}(r)). \quad (20)$$

Now, using the definition of the generalized Laguerre polynomial Equation 18, we can rewrite:[3]

$$\psi_{nlm}(r) = \sum_{k=0}^{n-l-1} \frac{N_{nl} p_0}{N_v^\zeta} \frac{(-1)^k}{k!} \binom{n+l}{n-l-1-k} \tilde{\chi}_{vlm}(\beta r). \quad (21)$$

Table 1. Relationship between Slater and Sturmian orbitals (simplest cases).

Sturmian orbital	Slater orbital
$\psi_{1,0,0}$	$\chi_{1,0,0}$
$\psi_{2,0,0}$	$\chi_{1,0,0} - \sqrt{3}\chi_{2,0,0}$
$\psi_{2,1,m}$	$\chi_{2,1,m}$
$\psi_{3,0,0}$	$\chi_{1,0,0} - 2\sqrt{3}\chi_{2,0,0} + \sqrt{10}\chi_{3,0,0}$
$\psi_{3,2,m}$	$\chi_{3,2,m}$

An equivalent expression is obtained expanding the Newton binomial and using the Pochhammer symbol:[8]

$$\psi_{nlm}(r) = \sum_{k=0}^{n-l-1} \frac{N_{nl}^{p_0}}{N_v^\zeta} \frac{(n+l)!}{(n-l-1)!(2l+1)!}$$

$$\times \frac{(-n+l+1)_k}{(2l+2)_k} \frac{\tilde{\chi}_{vlm}(\beta r)}{k!}. \quad (22)$$

In the last equation, we note that Slater orbitals in eq. 22 appear in the form $\tilde{\chi}_{vlm}$, where $v = k + l - 1$.

The eq. 22 can be used to circumvent the bottleneck in *ab initio* calculations with Sturmian orbitals exploiting progress in the machinery for integral calculations for Slater orbitals[11] and in view of the slow (but hopefully steady) advance rate in the fully analytical formulation and computational implementation of all integrals in the Sturmian representations. This program can be shown to be feasible in practice, in view of the fact that when we move to momentum space[12] by Fock projection (see next section), we exhibit the relationship between momentum space Sturmians[13] and hyperspherical harmonics, and the latter enjoy properties of representations[14] of Lie groups permitting the use of fully analytical machineries such as those exploited in quantum mechanical angular momentum theory. The following section is just a sketch with key references outlining the steps of this process and an assessment of present status.

4. Sturmians and hyperspherical harmonics as atomic and molecular orbitals

One of the main strengths associated with the use of Sturmian basis sets consists, as pointed out in many references (e.g., reference 7), is the complete reciprocity among these basis sets in the configuration space and their counterparts in momentum space, which can be mathematically identified with hyperspherical harmonics. The advantage of employing hyperspherical harmonics lies in the possibility of introducing alternative parameterizations, labelled by various quantum numbers, corresponding to different reduction schemes of the rotational O(d) group into its subgroups and to resort to the well-studied machinery developed for angular momentum algebra,[15] its generalizations[16] and its extensions to elliptic type coordinates.[17]

Thanks to the duality between configuration and momentum space, the same elements can be used to connect alternative Sturmian bases, arising from the separation of the hydrogen atom Schrödinger equation (Equation 1) in different sets of coordinates. This

provides a most powerful tool to be exploited for building up the most appropriate basis sets to solve multi-electron and/or multicentre problems. Moreover, this approach is completely general and can be extended to any dimension, allowing, for instance, the use of alternative basis sets to deal with the d-dimensional hydrogen atom,[18] though the usual S^3 Sturmians (and the corresponding O(4) hyperspherical harmonics) are most commonly employed in applications. Indeed, it is possible to build up different parameterizations of the O(4) sphere and classify them according to the rotation and angular momentum operators.[19,20] Thus, along with the O(4)⊃O(3)⊃O(2) reduction chain hyperspherical harmonics $Y_{nlm}(\chi, \theta, \varphi)$, counterpart in momentum space of the spherical Sturmian, an hyperspherical harmonic

$$Y_{n\mu m}(\Theta, \Phi, \varphi), = (-1)^{n-i}(i)^m (n/(2\pi^2))^{1/2}$$
$$\times \ D^{(n-1)/2}_{(\mu+m)/2,(\mu-m)/2}(-\Phi - \varphi, 2\Theta, \varphi - \Phi)$$

can be obtained, corresponding to a $O(4) \supset O(2) \times O(2)$ chain reduction, which is simultaneously in eigenstate for the angular momentum projection and the Runge-Lenz vector projection on the same z axis. Such an harmonic turns out to be the momentum space counterpart of the hydrogenoid Sturmian in parabolic coordinates. The connection between the two harmonics (and between the two hydrogenoid Sturmians) is essentially a Clebsch-Gordan coefficient (see, for example, reference [21]). Other hyperspherical harmonics can be obtained for $O(4)$, corresponding to the same kinds of reduction chain, but in eigenstate for different bi or tri-dimensional operators. Among them it is worth mentioning the lambda basis, whose corresponding harmonic $Y_{n,\lambda,m}$ is connected to the Y_{nlm} harmonic through a generalized $6j$ coefficient.[19,20]

These basis sets, though leading to the same results for problems with hyperspherical symmetry, behave very differently when the symmetry is partially broken, for example by the introduction of an electric and/or magnetic field. In this case parametrizations conserving the remnants of the surviving symmetry are particularly suited, the parabolic Sturmian provides solutions for the Stark effect in hydrogen atom, whereas the lambda basis (also called Zeeman basis) can be used for the hydrogen diamagnetism.[22] It is worth pointing out that, although in some cases the expression of the related Sturmian can be difficult to be explicitly worked out, it can be readily obtained by the corresponding easy-to-implement (generalized) angular momentum recoupling coefficient.[16,20] The quantum mechanics of atoms and molecules can also be discussed in terms of the breaking of the hyperspherical symmetry of a d-dimensional hydrogenoid atom, $d = 3(N - 1)$ for N

body Coulomb problems, due to the introduction of further charged particles (electrons and/or nuclei). Thus, in configuration space, Sturmian basis functions can be used as expansion basis sets to build up atomic and molecular orbitals.[23,24] Additionally, one can choose among alternative hyperspherical harmonics pertaining to different subgroup chain reductions of the original (d+1)-dimensional rotation group and thus possessing different symmetry properties. Benchmark calculations for 3-body problems (e.g., He and iso-electronic ions, H_2^+ beyond the Born – Oppenheimer approximation, $e^- e^+ e^-$), using alternative Sturmian basis sets with different symmetry properties, have been extensively carried out and their convergence properties critically analysed in terms of the relative weights of the involved particles in references [25] and [26]. Extension to molecules, starting from the early work of Shibuya and Wulfman, has been explored for the H_2^+ case study, in terms of one electron molecular orbitals to obtain secular equations for multicentre problems[27,28]. Again the use of alternative Sturmians (such as those obtained from the separation in parabolic and elliptic[29] coordinates) is fundamental to reach a fast convergence.[10]

5. Conclusions

This paper focused on configuration space and tried to establish some relationships between basis sets. The importance of identifying momentum space orbitals with hyperspherical harmonics, establishing connections with angular momentum algebra and promising the full analytical treatment of integrals and matrix elements occurring in quantum chemistry is also highlighted.

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