

Chapter 1

HISTORICAL BACKGROUND

1.1 Sturm-Liouville theory

Sturmians derive their name from Sturm-Liouville theory, a branch of mathematics founded by Jacques Charles François Sturm (1803-1855) and Joseph Liouville (1809-1882). The Sturm-Liouville equation, which is named after them, can be written in the form:

$$\left[\frac{d}{dr} \left(p(r) \frac{d}{dr} \right) - q(r) + \lambda_n w(r) \right] u_n(r) = 0 \quad (1.1)$$

Provided that boundary conditions of the form

$$\begin{aligned} u_n(a) \cos \alpha - p(a)u'(a) \sin \alpha &= 0 & 0 < \alpha < \pi \\ u_n(b) \cos \beta - p(b)u'(b) \sin \beta &= 0 & 0 < \beta < \pi \end{aligned} \quad (1.2)$$

are imposed on a set of solutions to the Sturm-Liouville equation, and provided that $p(x)$ is differentiable, with $q(x)$ and $w(x)$ continuous, $p(x) > 0$ and $w(x) > 0$ in the interval $a < x < b$, it can be shown that

$$(\lambda_{n'}^* - \lambda_n) \int_a^b dr u_{n'}^*(r) w(r) u_n(r) = 0 \quad (1.3)$$

From (1.3) it can be seen that the eigenvalues λ_n are real and that the eigenfunctions corresponding to different eigenvalues are orthogonal under an inner product weighted by $w(r)$, i.e.,

$$\int_a^b dr u_n^*(r) w(r) u_{n'}(r) = 0 \quad \text{if } \lambda_{n'} \neq \lambda_n \quad (1.4)$$

Furthermore, if the conditions mentioned above are satisfied, it can be shown that the eigenvalues are well ordered with

$$\lambda_1 < \lambda_2 < \lambda_3 < \lambda_3 < \cdots < \lambda_n < \cdots \rightarrow \infty \quad (1.5)$$

Each eigenvalue λ_n is uniquely associated with an eigenfunction $u_n(r)$ which has exactly $n - 1$ nodes in the range $a < x < b$. The eigenfunctions $u_n(r)$ can be normalized in such a way that

$$\int_a^b dr u_{n'}^*(r)w(r)u_n(r) = \delta_{n',n} \quad (1.6)$$

so that they form the orthonormal basis of a Hilbert space with weighting function $w(r)$. All second-order ordinary differential equations can be transformed into the Sturm-Liouville equation.

1.2 The introduction of Sturmians into quantum theory

One of the very early triumphs of quantum theory was the exact solution of the Schrödinger equation for hydrogenlike atoms. It was natural to try to use hydrogenlike orbitals as building blocks to represent the wave functions of more complicated atoms. However, it was soon realized that the cusps needed for accurate representation of (for example) the wave functions of heliumlike atoms and ions would require the inclusion of the continuum if the basis were to be built up of hydrogenlike orbitals. The continuum proved to be prohibitively difficult to use in practical calculations. This dilemma led Høloien, Shull and Löwdin [Shull and Löwdin, 1959] to introduce radial functions of the form

$$R_{n,l}(r) = \frac{u_{n,l}(r)}{r} \quad (1.7)$$

where $u_{n,l}(r)$ satisfied

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \frac{k^2}{2} + \frac{kn}{r} \right] u_{n,l}(r) = 0 \quad n = 1, 2, 3, \dots \quad (1.8)$$

Here k is held constant for all the members of the basis set. Shull and Löwdin were able to show that with basis sets using radial functions of this type, correct representation of the cusps could be achieved without the inclusion of the continuum. Other early authors who used functions of this type in quantum theory included Midtdal and Rotenberg [Rotenberg, 1962,1970]. Rotenberg gave the name ‘‘Sturmians’’ to these functions in order to call attention to their connection with Sturm-Liouville theory. The reader can verify that with the substitutions

$$\begin{aligned} p(r) &\rightarrow 1 \\ q(r) &\rightarrow \frac{k^2}{2} + \frac{l(l+1)}{r^2} \end{aligned}$$

$$\lambda_n w(r) \rightarrow \frac{kn}{r} \quad (1.9)$$

the Sturm-Liouville equation reduces to equation (1.8).

It is interesting to notice that the Sturm-Liouville equation has sufficient flexibility to represent both the conventional type of eigenvalue equation encountered in quantum theory, where the eigenvalues λ_n are associated with the energy, and also what might be called “conjugate eigenvalue problems”, where the eigenvalues λ_n are weighting factors by which the potential energy is multiplied in order to make all of the solutions correspond to a particular energy E .

1.3 One-electron Coulomb Sturmians

Rotenberg defined Sturmians as solutions of

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + E - \lambda_{n,l} V_0(r) \right] u_{n,l}(r) = 0 \quad (1.10)$$

for any $V_0(r)$ that is negative over the range $a < r < b$. For the particular set of Sturmians used by Shull and Löwdin, $E - \lambda_{n,l} V_0(r)$ has the form shown in equation (1.8), and basis sets of this type have come to be called “Coulomb Sturmians”. One-electron Coulomb Sturmians have exactly the same form as the familiar hydrogenlike orbitals, except that the factor Z/n which appears in the hydrogenlike radial functions is replaced by a factor k , which is the same for all the members of the basis set. They can be written in the form

$$\chi_{nlm}(\mathbf{x}) = R_{nl}(r) Y_{lm}(\theta, \phi) \quad (1.11)$$

where $Y_{lm}(\theta, \phi)$ is a spherical harmonic and

$$R_{nl}(r) = \mathcal{N}_{nl} (2kr)^l e^{-kr} F(l+1-n|2l+2|2kr) \quad (1.12)$$

with

$$\mathcal{N}_{nl} = \frac{2k^{3/2}}{(2l+1)!} \sqrt{\frac{(l+n)!}{n(n-l-1)!}} \quad (1.13)$$

In equation (1.12), $F(a|b|x)$ is a confluent hypergeometric function defined by

$$F(a|b|x) \equiv \sum_{k=0}^{\infty} \frac{a^{\bar{k}}}{k! b^{\bar{k}}} x^k = 1 + \frac{a}{b} x + \frac{a(a+1)}{2b(b+1)} x^2 + \dots \quad (1.14)$$

The first few Coulomb Sturmian radial functions are shown in Table 1.1 at the end of the chapter. Since the Coulomb Sturmians have the same form as the hydrogenlike orbitals with Z/n replaced by k , they must obey the hydrogenlike Schrödinger equation with the same substitution. In atomic units this becomes

$$\left[-\frac{1}{2}\nabla^2 + \frac{1}{2}k^2 - \frac{nk}{r}\right]\chi_{nlm}(\mathbf{x}) = 0 \quad (1.15)$$

For another member of the Coulomb Sturmian basis set we have

$$\left[-\frac{1}{2}\nabla^2 + \frac{1}{2}k^2 - \frac{n'k}{r}\right]\chi_{n'l'm'}(\mathbf{x}) = 0 \quad (1.16)$$

From (1.15) and (1.16) we can obtain the relationships

$$\int d^3x \chi_{n'l'm'}^*(\mathbf{x}) \left[-\frac{1}{2}\nabla^2 + \frac{1}{2}k^2\right]\chi_{nlm}(\mathbf{x}) = \int d^3x \chi_{n'l'm'}^*(\mathbf{x}) \frac{nk}{r} \chi_{nlm}(\mathbf{x}) \quad (1.17)$$

and

$$\int d^3x \chi_{nlm}(\mathbf{x}) \left[-\frac{1}{2}\nabla^2 + \frac{1}{2}k^2\right]\chi_{n'l'm'}^*(\mathbf{x}) = \int d^3x \chi_{nlm}(\mathbf{x}) \frac{n'k}{r} \chi_{n'l'm'}^*(\mathbf{x}) \quad (1.18)$$

If we subtract (1.18) from (1.17), making use of the Hermiticity of the Laplacian operator, we have

$$(n - n') \int d^3x \chi_{n'l'm'}^*(\mathbf{x}) \frac{1}{r} \chi_{nlm}(\mathbf{x}) = 0 \quad (1.19)$$

so that

$$\int d^3x \chi_{n'l'm'}^*(\mathbf{x}) \frac{1}{r} \chi_{nlm}(\mathbf{x}) = 0 \quad \text{if } n \neq n' \quad (1.20)$$

Finally, using the fact that the hydrogenlike orbitals obey the Virial theorem, and also making use of the orthonormality of the spherical harmonics we obtain

$$\int d^3x \chi_{n'l'm'}^*(\mathbf{x}) \frac{1}{r} \chi_{nlm}(\mathbf{x}) = \frac{k}{n} \delta_{n'n} \delta_{l'l} \delta_{m'm} \quad (1.21)$$

which is the potential-weighted orthonormality relation obeyed by Coulomb Sturmian basis sets.

1.4 Generalized Sturmians and many-particle problems

In a pioneering 1968 paper, Osvaldo Goscinski [Goscinski, 1968, 2003] generalized the concept of Sturmians. He regarded Sturmians as isoenergetic solutions to a general d -dimensional Schrödinger-like equation of the form

$$\left[-\frac{1}{2}\Delta + \beta_\nu V_0(\mathbf{x}) - E_\kappa \right] \Phi_\nu(\mathbf{x}) = 0 \quad (1.22)$$

with a weighted potential $\beta_\nu V_0(\mathbf{x})$, the weighting constants β_ν being chosen in such a way as to make all of the solutions correspond to the same energy, E_κ . Equation (1.22) could be applied to N particles of different masses m_j with

$$\Delta \equiv \sum_{j=1}^N \frac{1}{m_j} \nabla_j^2 \quad (1.23)$$

For a collection of N electrons, one can let

$$\Delta \equiv \sum_{j=1}^d \frac{\partial^2}{\partial x_j^2} \quad (1.24)$$

where $d = 3N$ and

$$\mathbf{x} = (x_1, x_2, \dots, x_d) \quad (1.25)$$

since, in atomic units, $m_j = 1$ for all the electrons. Goscinski was able to show (by an argument similar to equations (1.15)-(1.21)), that generalized Sturmians obey a potential-weighted orthogonality relation of the form

$$\int dx \Phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) = 0 \quad \text{if } \beta_{\nu'} \neq \beta_\nu \quad (1.26)$$

We should notice that in equations (1.22) and (1.26), ν stands for a set of quantum numbers, some of which influence the value of β_ν , while others do not. We can call these respectively *major* and *minor* quantum numbers. Orthogonality with respect to the minor quantum numbers can often be established by means of symmetry properties. When this is not possible, the members of a Sturmian basis set can be made orthogonal with respect to the remaining minor quantum numbers by means of for example Graham-Schmidt or Löwdin orthogonalization. We shall normalize our generalized Sturmian basis sets in such a way that the potential-weighted orthonormality relations take the form

$$\int dx \Phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \Phi_\nu(\mathbf{x}) = -\delta_{\nu',\nu} \frac{p_\kappa^2}{\beta_\nu} \quad (1.27)$$

where

$$p_\kappa^2 \equiv -2E_\kappa \quad (1.28)$$

This type of normalization is convenient because

- (1) It makes (1.27) reduce to (1.21) for the case of Coulomb Sturmians (with $d = 3$, $p_\kappa = k$ and $\beta_\nu = nk$).
- (2) It makes the generalized Sturmians fit more naturally into the theory of Sobolev spaces.
- (3) The special Goscinskian configurations, which will be introduced in Chapter 3, are already properly normalized.

1.5 Use of generalized Sturmian basis sets to solve the many-particle Schrödinger equation

The non-relativistic many-particle Schrödinger equation can be written in the form

$$\left[-\frac{1}{2}\Delta + V(\mathbf{x}) - E_\kappa \right] \Psi_\kappa(\mathbf{x}) = 0 \quad (1.29)$$

where atomic units are used and where Δ is defined by (1.23) or (1.24). We now expand the wave function $\Psi_\kappa(\mathbf{x})$ in terms of a generalized Sturmian basis set.

$$\Psi_\kappa(\mathbf{x}) = \sum_\nu \Phi_\nu(\mathbf{x}) B_{\nu,\kappa} \quad (1.30)$$

Substituting this expansion into the Schrödinger equation, and using the fact that all the members of our basis set obey equation (1.22), we obtain

$$\begin{aligned} & \sum_\nu \left[-\frac{1}{2}\Delta + V(\mathbf{x}) - E_\kappa \right] \Phi_\nu(\mathbf{x}) B_{\nu,\kappa} \\ &= \sum_\nu [V(\mathbf{x}) - \beta_\nu V_0(\mathbf{x})] \Phi_\nu(\mathbf{x}) B_{\nu,\kappa} = 0 \end{aligned} \quad (1.31)$$

If we multiply (1.31) on the left by a conjugate function from our basis set and integrate over all the coordinates, we obtain

$$\sum_\nu \int dx \Phi_{\nu'}^*(\mathbf{x}) [V(\mathbf{x}) - \beta_\nu V_0(\mathbf{x})] \Phi_\nu(\mathbf{x}) B_{\nu,\kappa} = 0 \quad (1.32)$$

We next introduce the notation

$$T_{\nu',\nu} \equiv -\frac{1}{p_\kappa} \int dx \Phi_{\nu'}^*(\mathbf{x}) V(\mathbf{x}) \Phi_\nu(\mathbf{x}) \quad (1.33)$$

Finally, making use of the potential-weighted orthonormality relations (1.27), we obtain the Sturmian secular equations.

$$\sum_\nu [T_{\nu',\nu} - p_\kappa \delta_{\nu',\nu}] B_{\nu,\kappa} = 0 \quad (1.34)$$

These secular equations have several remarkable features that will be discussed in more detail in later chapters. For the moment, it is interesting to notice that the kinetic energy term has disappeared. Furthermore, the eigenvalues are not energies, but values of the “scaling parameter” p_κ , which is related to the energy spectrum through equation (1.28).

Table 1.1: One-electron Coulomb Sturmian radial functions. If k is replaced by Z/n they are identical to the familiar hydrogenlike radial wave functions.

n	l	$R_{n,l}(r)$
1	0	$2k^{3/2}e^{-kr}$
2	0	$2k^{3/2}(1 - kr)e^{-kr}$
2	1	$\frac{2k^{3/2}}{\sqrt{3}} kr e^{-kr}$
3	0	$2k^{3/2} \left(1 - 2kr + \frac{2(kr)^2}{3} \right) e^{-kr}$
3	1	$2k^{3/2} \frac{2\sqrt{2}}{3} kr \left(1 - \frac{kr}{2} \right) e^{-kr}$
3	2	$2k^{3/2} \frac{\sqrt{2}}{3\sqrt{5}} (kr)^2 e^{-kr}$