# ON THE STURM–LIOUVILLE EQUATION WITH TWO-POINT BOUNDARY CONDITIONS

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*ABSTRACT.* In numerical solution of a Sturm–Liouville system, it is necessary to determine an eigenvalue by a method of successive approximation. A relation is derived between the estimated accuracy of an approximate eigenvalue and the accuracy at every point of its corresponding eigenfunction. A method is also described whereby the correction to a trial eigenvalue, required for convergence to its true value, can be automatically determined. This method has been successfully used in solving radial wave-function equations, both with and without 'exchange', arising from the Hartree–Slater–Fock analysis of Schrödinger's equation.

1. *An accuracy relation.* Let us consider the differential equation of a Sturm–Liouville system (1)

$$P''(x)+[g(x)+\lambda f(x)]P(x)=0, \tag{1}$$

where, in a range $x_0 \leqslant x \leqslant x_n$, $f$ and $g$ are known functions of $x$ and there exists a $P(x)$ for each value of $\lambda$. We may assume, without loss of generality, that $P(x_0)=0$. Regarded as functions of $\lambda$, the solutions $P(x,\lambda)$ of this equation form a continuum, and we can differentiate (1) with respect to $\lambda$. We have then

$$\partial P''/\partial\lambda+(g+\lambda f)(\partial P/\partial\lambda)+fP=0. \tag{2}$$

If we multiply (1) by $\partial P/\partial\lambda$, and subtract (2) multiplied by $P$, we may write the result as

$$\frac{\partial}{\partial x}\left[P'\frac{\partial P}{\partial\lambda}-P\frac{\partial P'}{\partial\lambda}\right]=fP^2. \tag{3}$$

Integrating (3) between $x_0$ and some point $X$, where $x_0 \leqslant X \leqslant x_n$, we have

$$\left.\begin{aligned}\left[P'\frac{\partial P}{\partial\lambda}-P\frac{\partial P'}{\partial\lambda}\right]_{x_0}^{X}&=\int_{x_0}^{X}fP^2dx,\\ \text{or}\qquad \left[P^2\frac{\partial}{\partial\lambda}(P'/P)\right]_{x_0}^{X}&=\int_{x_0}^{X}fP^2dx.\end{aligned}\right\} \tag{4}$$

Since $P(x_0)=0$, we have

$$P^2(X)\left[\frac{\partial}{\partial\lambda}(P'/P)\right]_{x=X}=\int_{x_0}^{X}fP^2dx. \tag{5}$$

If we replace the derivative with respect to $\lambda$ by finite differences, we find that

$$P^2(X)\,\Delta(P'/P)_{x=X}=\Delta\lambda\int_{x_0}^{X}fP^2dx+O(\Delta\lambda^2). \tag{6}$$

Let us now consider a solution $P_t(x)$ of equation (1) corresponding to a value $\lambda=\lambda(t)$. Suppose that, by some numerical process, we obtain an approximation $P_c(x)$ to this solution corresponding to an approximate value of $\lambda(t)$ which we call $\lambda(c)$. If we can

estimate $\Delta\lambda = \lambda(c) - \lambda(t)$, then we can compute the error in $P'/P$ at each point $X$, where $x_0 < X \leqslant x_n$, from equation (6); for we have

$$\Delta(P_c'/P_c)_{x=X} = \Delta\lambda \int_{x_0}^{X} f[P_c(x)/P_c(X)]^2\, dx + O(\Delta\lambda^2), \tag{7}$$

where

$$\Delta(P_c'/P_c)_{x=X} \equiv (P_c'/P_c - P_t'/P_t)_{x=X}.$$

We note that the value of the error is indeterminate near the nodes of $P_c$, and we must have recourse to equation (4) in these regions. This equation yields

$$P_c'(X)\,\Delta P_c(X) = \Delta\lambda \int_{x_0}^{X} f P_c^2\, dx + O(\Delta\lambda^2) + O[P_c(X)]. \tag{8}$$

If $P(x_0) = 0$ and $P(x_n)$ tends to zero as $x_n$ tends to infinity, the values of $\lambda$ for which a solution is possible are restricted to a set of discrete eigenvalues. It has been shown by Gregory (2) that bounds can be generally set upon $\Delta\lambda$ in this case. If solution is carried out numerically by replacing the derivative $P''$ by a difference, equivalent to order $s$, Gregory has further shown that the value of $\Delta\lambda$ corresponding to the process used can be determined to order $(\Delta x)^s$. From (7) and (8) we may thus determine the difference between $P_c'/P_c$ and $P_t'/P_t$ at every point to any specified order of accuracy.

An important application of the analysis given above is to the Sturm–Liouville equations for radial wave functions which arise from the Hartree–Slater analysis (3) of the Schrödinger equation for electrons in atoms. For this case $f = 1$, $x_0 = 0$, and $x_n$ is a value of $x$ so large that $P_t'$, $P_t$ can be accurately evaluated by a series expansion. The value of $\lambda(t)$ is an approximation to an observed spectral energy level, $\lambda(o)$, which can be measured very accurately. Since the equation represents only approximately the physical situation considered, $\lambda(c) - \lambda(o)$ contains errors due to the derivation of the equation as well as computational errors. Nevertheless, we may (with suitable reservations) take $\lambda(c) - \lambda(o)$ as an estimate of $\Delta\lambda$ in order to give a measure of the difference between $P_c'/P_c$, derived by some process of solution of the equation, and $P_t'/P_t$. The magnitude of this difference is one possible measure of accuracy of the solution obtained and is sometimes a useful criterion by which to judge the correctness of that solution. (For further discussion of possible criteria see James and Coolidge (7).)

2. *Automatic eigenvalue adjustment.* If the solution of the radial wave equation

$$P'' + (\lambda + g)\,P = 0, \quad \text{where} \quad P(0) = P(x_n) = 0, \tag{9}$$

is carried out by an iterative procedure, such as that described by Hartree (4), it is desirable to set up a method of adjusting the trial parameter $\lambda_r$ used for each iteration. The iterative system employed is to integrate outwards from $x = 0$ to $x = X$, where $0 < X < x_n$, and then integrate inwards from $x_n$ to $X$, and compare the values of $P'/P$ at $X$ for outward and inward integrations respectively; the process is repeated with revised $\lambda$ values, but the same starting values for $P$, $P'$, until adequate agreement is obtained at $X$. Let us write $Q_r(x)$ for the calculated values of $P(x)$ found by outward integration for the $r$th iteration, and $R_r(x)$ for the corresponding values of $P(x)$ obtained

from inward integration. We denote by $D_r(X)$ the difference $(Q_r'/Q_r - R_r'/R_r)_{x=X}$. From (6) we may write

$$\left.\begin{aligned} Q_r^2(X)\,\partial/\partial\lambda\,(Q_r'/Q_r)_{x=X} &= \int_0^X Q_r^2\,dx, \\ R_r^2(X)\,\partial/\partial\lambda(R_r'/R_r)_{x=X} &= -\int_X^{x_n} R_r^2\,dx. \end{aligned}\right\} \tag{10}$$

Clearly we may replace the derivative in either case by finite differences, and thus may obtain, for instance, to the first order in $\Delta\lambda_r$, the equation

$$\Delta\lambda_r = -R_r^2(X)\,\Delta(R_r'/R_r)_{x=X} \Big/ \int_X^{x_n} R_r^2\,dx. \tag{11}$$

The value of $\Delta(R_r'/R_r)_{x=X}$ is not known, but we can approximate to this by the amount of correction required in $R_r'/R_r$. This is approximately $D_r(X)$, or may be taken as some combination of this and the previous corrections $D_{r-1}(X)$, etc.

Writing $\Delta(R_r'/R_r)_{x=X} = KD_r(x)$, and assuming that the value of $\int_X^{x_n}[R_r(x)/R_r(X)]^2\,dx$ remains approximately independent of $r$, equation (11) becomes

$$\Delta\lambda_r \doteqdot KD_r(X). \tag{12}$$

The assumption made is usually justified if $X$ is taken not too far from $x_n$.

The iterative process established by taking $\lambda = \lambda_1$, integrating (9) to find $D_1(x)$, then taking $\lambda_2 = \lambda_1 + \Delta\lambda_1$ and repeating this process until $D_r(x)$, $\Delta\lambda_r$ are small, will converge if $|\Delta\lambda_{r+1}/\Delta\lambda_r| < 1$ and hence if $|D_{r+1}(X)/D_r(X)| < 1$. From (10) we may obtain, by adding and replacing differentials by differences,

$$\Delta D_r = \Delta\lambda_r N_r^2 + O(\Delta\lambda_r^2), \tag{13}$$

where $$N_r^2 \equiv \int_0^X [Q_r(x)/Q_r(X)]^2\,dx + \int_X^{x_n} [R_r(x)/R_r(X)]^2\,dx.$$

Using (12) to replace $\Delta\lambda_r$ in this equation, we have, neglecting $O(\Delta\lambda_r^2)$, the equation

$$D_{r+1}(X) = D_r(X)\,[1 - KN_r^2].$$

For convergence of the process, it follows that we require $0 < K < 2/N_r^2$; and the process will converge most rapidly if $K \doteqdot 1/N_r^2$. We may thus rewrite (11) as

$$\Delta\lambda_r \doteqdot -R_r^2(X)\,D_r(X)/N_r^2 \int_X^{x_n} R_r^2\,dx. \tag{14}$$

3. *Applications.* Equation (14) has been used on the EDSAC at the University Mathematical Laboratory, Cambridge, for Sturm–Liouville equations arising from atomic wave-function calculations, such as those for the thallium ions described by Douglas, Hartree, and Runciman (5). It has also been successfully employed for wave functions computed with exchange for $Si^+$ (3) and $Ca^+$ (6), although the radial equations are not strictly of Sturm–Liouville type (see, for example, (4)). The initial value, $\lambda_1$, was chosen to be the observed value, $\lambda(o)$, for the state being investigated. It was not generally found necessary to use a high-order process for convergence, since the process

described above is sufficiently rapid for the integro-differential equations involved in computing a radial wave function without 'exchange'. For computation involving exchange integrals, it is less important, in the early stages of computation, to adjust $\lambda$ very accurately than to obtain consistent values for the integrals in the potential function and in the exchange term. The wave functions in the $d$ shell, for instance, are especially sensitive to small changes in the values for these integrals. A rapid convergence technique for $\lambda$ is thus secondary to good estimation of these integrals on the basis of former values obtained from previous iterations.

The point $X$ at which the results of the inward and outward integrations are to be matched, was found empirically by Hartree to be best chosen near the inflexion point of $P(x)$ with largest $x$. For this choice of $X$ the author found it best to use (14) to calculate $\Delta\lambda_r$ rather than one of the other possible equations which can be derived from (10), since $\int_X^{x_n} [R_r(x)/R_r(X)]^2\,dx$ does not change rapidly with $\lambda$, and thus remains approximately independent of $r$.

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