

F Discretization and Quadrature Schemes

As a first-order differential equation, the radial Dirac equation, which is the central equation to be solved in the case of atoms, requires a discretization scheme, and several options are at hand of which some should be presented here for the sake of completeness. The first one is analogous to the Numerov procedure for second-order differential equations without first derivatives [404,405]. The derivation in terms of Taylor series expansions provides a derivation which is easier to understand. However, using operator techniques is the most elegant way for this particular task.

F.1 Numerov Approach toward Second-Order Differential Equations

A general second-order differential equation of the form

$$\chi''(s) + F(\epsilon, s)\chi(s) = G(s) \quad (\text{F.1})$$

can be discretized on an equidistant grid of step size h , for instance, by the so-called Numerov method [406, 407, 409, 412, 972, 973]. The special feature of this method is that the truncation error is of comparatively high order in the step size h while only three points are required to discretize the second derivative. This is achieved through the explicit use of Eq. (F.1) as we shall see in the following.

For this, we expand the function $\chi(s_p) = \chi_p$ at grid point s_p and its second derivative χ_p'' at that grid point into a Taylor series

$$\chi_{p\pm 1} = \chi(s_p \pm h) = \chi_p \pm \frac{1}{1!}\chi_p' h + \frac{1}{2!}\chi_p'' h^2 \pm \frac{1}{3!}\chi_p''' h^3 + \dots \quad (\text{F.2})$$

$$\chi_{p\pm 1}'' = \chi(s_p \pm h)'' = \chi_p'' \pm \frac{1}{1!}\chi_p''' h + \frac{1}{2!}\chi_p^{(4)} h^2 \pm \frac{1}{3!}\chi_p^{(5)} h^3 + \dots \quad (\text{F.3})$$

Addition of Eq. (F.2) — and similarly for Eq. (F.3) — leads to

$$\chi_{p-1} + \chi_{p+1} = 2\chi_p + \chi_p'' h^2 + \frac{1}{12}\chi_p^{(4)} h^4 + O(h^6) \quad (\text{F.4})$$

and

$$\chi''_{p-1} + \chi''_{p+1} = 2\chi''_p + \chi_p^{(4)}h^2 + O(h^4) \tag{F.5}$$

If the second derivative of χ in Eq. (F.5) is replaced by the right-hand side of the re-arranged Eq. (F.1)

$$\chi'' = G - F\chi \tag{F.6}$$

and if we solve for $\chi_p^{(4)}$, we obtain

$$h^2\chi_p^{(4)} = G_{p-1} - 2G_p + G_{p+1} - F_{p-1}\chi_{p-1} + 2F_p\chi_p - F_{p+1}\chi_{p+1} + O(h^4) \tag{F.7}$$

Now, Eq. (F.7) is applied to delete $\chi_p^{(4)}$ from Eq. (F.4). Solving for χ''_p then yields

$$\begin{aligned} \chi''_p &= \left(\frac{1}{h^2} + \frac{F_{p-1}}{12}\right)\chi_{p-1} - 2\left(\frac{1}{h^2} + \frac{F_p}{12}\right)\chi_p + \left(\frac{1}{h^2} + \frac{F_{p+1}}{12}\right)\chi_{p+1} \\ &\quad - \frac{1}{12}(G_{p-1} - 2G_p + G_{p+1}) + O(h^4) \end{aligned} \tag{F.8}$$

Insertion of this result in the original differential equation yields a set of linear equations whose p -th equation reads

$$\begin{aligned} \left(\frac{1}{h^2} + \frac{F_{p-1}}{12}\right)\chi_{p-1} - \left(\frac{2}{h^2} - \frac{10F_p}{12}\right)\chi_p + \left(\frac{1}{h^2} + \frac{F_{p+1}}{12}\right)\chi_{p+1} \\ = \frac{1}{12}(G_{p-1} + 10G_p + G_{p+1}) + O(h^4) \end{aligned} \tag{F.9}$$

Multiplication by h^2 and introduction of the definitions

$$b_p \equiv 1 + \frac{h^2}{12}F_p, \quad a_p \equiv -2 + \frac{10h^2}{12}F_p = 10b_p - 12 \tag{F.10}$$

and

$$d_p \equiv \frac{h^2}{12}(G_{p-1} + 10G_p + G_{p+1}) \tag{F.11}$$

finally yields

$$a_{p-1}\chi_{p-1} + b_p\chi_p + a_{p+1}\chi_{p+1} = b_p \tag{F.12}$$

All such equations can be collected in a single matrix equation that reads

$$\begin{pmatrix} a_1 & b_2 & & & 0 \\ b_1 & a_2 & b_3 & & \\ & b_2 & a_3 & b_4 & \\ & & \ddots & \ddots & \ddots \\ & & & b_{n-2} & a_{n-1} & b_n \\ 0 & & & & b_{n-1} & a_n \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \\ \chi_3 \\ \vdots \\ \chi_{n-1} \\ \chi_n \end{pmatrix} = \begin{pmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ d_{n-1} \\ d_n \end{pmatrix} \tag{F.13}$$

Note that the boundaries would have to be corrected via simple extrapolation in order to preserve the numerical accuracy wanted. The determinant of the matrix in Eq. (F.13) can be calculated by a Sturm chain and the eigenvalue is then solved for by bisection [408,974].

F.2 Numerov Approach for First-Order Differential Equations

We now turn to the discretization of the coupled first-order differential equations as they occur in the solution of the Dirac radial equation for atoms (see chapter 9). While the Numerov scheme is well established for second-order differential equations — and, hence, for the solution of the radial Schrödinger equation for atoms — this is not the case for first-order differential equations. Indeed, it was long believed that the Numerov scheme cannot be used at all in this context [973].

We again denote as $\chi(s)$ the function to be discretized on an equidistant grid in the variable s . The differential equation to be solved reads

$$\frac{1}{a}\chi'(s) + F(s)\chi(s) = G^*(s) \tag{F.14}$$

where a can take the values ± 1 to account for the different signs of the first derivatives in the coupled Dirac–Hartree–Fock equations. h is the step size of the equidistant grid and the index p denotes the p -th grid point at s_p . To keep the equations clearly and simply arranged, $\chi(s_p)$ will be abbreviated as χ_p .

Note that the derivations will be held as general as possible. Thus, the coefficient functions of the coupled Dirac–Hartree–Fock equations, Eqs. (9.237) and (9.238), connected at a time with the other radial function are implicitly introduced via the inhomogeneity,

$$G^*(s) = G(s) - F_{UL}(s) y_L(s) \tag{F.15}$$

$$H^*(s) = H(s) - aF_{LU}(s) y_U(s) \tag{F.16}$$

The function $\chi(s)$ is assumed to be analytic. We should, however, note that the requirement of infinite differentiability is the reason for numerical problems with the untransformed non-analytic radial functions in calculations with point nuclei (cf. the non-integral exponent in the short-range series expansions derived in section 9.6.1). An analytic function $\chi(s)$ can be expanded into a Taylor series around grid point p ,

$$\chi_{p\pm 1} = \chi_p \pm \frac{1}{1!}\chi'_p h + \frac{1}{2!}\chi''_p h^2 \pm \frac{1}{3!}\chi'''_p h^3 + \dots \tag{F.17}$$

which may be subtracted from each other to become

$$-\chi_{p-1} + \chi_{p+1} = 2\chi'_p h + \frac{1}{3}\chi'''_p h^3 + O(\chi^{(5)}_p h^5) \tag{F.18}$$

where we use E. Landau's O -symbolism to indicate that the main term of the truncated series is of fifth order in h and contains a fifth derivative of $\chi(s)$ at grid point p . Note that every second term in the series expansion vanishes. The same procedure has to be repeated for the first derivative $\chi'(s)$, which yields the series expansions

$$\chi'_{p\pm 1} = \chi'_p \pm \frac{1}{1!}\chi''_p h + \frac{1}{2!}\chi'''_p h^2 \pm \frac{1}{3!}\chi^{(4)}_p h^3 + \dots \quad (\text{F.19})$$

which can be added to obtain

$$\chi'_{p-1} + \chi'_{p+1} = 2\chi'_p + \chi'''_p h^2 + O(\chi_p^{(5)} h^4) \quad (\text{F.20})$$

This equation may be rearranged to

$$\chi'''_p h^2 = \chi'_{p-1} - 2\chi'_p + \chi'_{p+1} + O(\chi_p^{(5)} h^4) \quad (\text{F.21})$$

which yields with the discretized differential equation (cf. Eq. (F.14))

$$\chi'_p = a(-F_p \chi_p + G_p^*) \quad (\text{F.22})$$

the expression

$$\begin{aligned} \chi'''_p h^2 = a \left[(G_{p-1}^* - F_{p-1} \chi_{p-1} - 2(G_p^* - F_p \chi_p) \right. \\ \left. + G_{p+1}^* - F_{p+1} \chi_{p+1}) \right] + O(\chi_p^{(5)} h^4) \end{aligned} \quad (\text{F.23})$$

for the unknown term $h/3 (\chi'''_p h^2)$ needed in Eq. (F.18). This equation then becomes, after division by $(2h)$, the discretized first derivative

$$\begin{aligned} \chi'_p = \left(-\frac{1}{2h} + \frac{a}{6} F_{p-1} \right) \chi_{p-1} - \frac{a}{3} F_p \chi_p + \left(\frac{1}{2h} + \frac{a}{6} F_{p+1} \right) \chi_{p+1} \\ - \frac{a}{6} G_{p-1}^* + \frac{a}{3} G_p^* - \frac{a}{6} G_{p+1}^* + O(\chi_p^{(5)} h^4) \end{aligned} \quad (\text{F.24})$$

where, if we use Eq. (F.22) for a second time and remove the division by $(2h)$, the final result (i.e., the discretized differential equation) will be

$$\begin{aligned} \left(-1 + \frac{ah}{3} F_{p-1} \right) \chi_{p-1} + \frac{4ah}{3} F_p \chi_p + \left(1 + \frac{ah}{3} F_{p+1} \right) \chi_{p+1} \\ = \frac{ah}{3} G_{p-1}^* + \frac{4ah}{3} G_p^* + \frac{ah}{3} G_{p+1}^* + O(\chi_p^{(5)} h^5) \end{aligned} \quad (\text{F.25})$$

Remember that a can take the values ± 1 only! Obviously, without using the differential equation, we obtain from Eqs. (F.18) and (F.21), the general expression

$$\begin{aligned} \chi_{p+1} - \chi_{p-1} &= 2\chi'_p h + \frac{h}{3} (\chi'_{p-1} - 2\chi'_p + \chi'_{p+1}) + O(\chi_p^{(5)} h^5) \\ &= \frac{h}{3} (\chi'_{p-1} + 4\chi'_p + \chi'_{p+1}) + O(\chi_p^{(5)} h^5) \end{aligned} \quad (\text{F.26})$$

F.3
Simpson's Quadrature Formula

For the numerical evaluation of expectation values, numerical quadrature schemes are needed. In the case of atoms (see chapter 9), these are one-dimensional and, hence, particularly simple. As an example, we discuss Simpson's rule in the following.

The famous Simpson rule for numerical quadrature can be written as [392, p.102]

$$\int_{s_{p-1}}^{s_{p+1}} f(s) ds = \frac{h}{3} [f(s_{p+1}) + 4f(s_p) + f(s_{p-1})] - \frac{h}{90} \delta^4 f(s_p) + O(h\delta^6 f(s)) \tag{F.27}$$

where the operator for a central difference, δ , is defined as $\delta f(x) = f(x + h/2) - f(x - h/2)$. If we rewrite this equation in terms of the integrated function $\chi(s) = \int f(s) ds$ we obtain

$$\chi(s_{p+1}) - \chi(s_{p-1}) = h/3 [\chi'(s_{p+1}) + 4\chi'(s_p) + \chi'(s_{p-1})] - \frac{h}{90} \delta^4 \chi'(s_p) + O[h\delta^6 \chi'(s)] \tag{F.28}$$

and get Eq. (F.26) — which will lead to Eq. (F.25) if the differential Eq. (F.22) is introduced to remove the derivatives of $\chi(s)$.

F.4
Bickley's Central-Difference Formulae

Simple discretization schemes use derivatives of Lagrangian interpolation polynomials that approximate the function known only at the grid points $\{s_i\}$. These schemes consist of tabulated numbers multiplied by the function's values at m contiguous grid points and are referred to as "m-point-formulae" by Bickley [411] (cf. [381, p. 914]). The accuracy of the numerical differentiation increases with the number of neighboring grid points needed. For an acceptable truncation error $O(h^t)$, $t = 4$ or higher, m is larger than t , which leads to an extended amount of computation. The general structure and usage of Bickley's central-difference formulae can be demonstrated for the simplest approximation of a first-order derivative,

$$\frac{df(s)}{ds} = \lim_{\Delta s \rightarrow 0} \frac{\Delta f(s)}{\Delta s} \tag{F.29}$$

which becomes for an equidistant grid $h = s_{k+1} - s_k$ at a given position s_k

$$\lim_{\Delta s \rightarrow 0} \frac{\Delta f(s)}{\Delta s} \Big|_{s=s_k} \approx \frac{f(s_{k+1}) - f(s_k)}{s_{k+1} - s_k} = \frac{1}{h} (-1, 1) \cdot \begin{pmatrix} f(s_k) \\ f(s_{k+1}) \end{pmatrix} \quad (\text{F.30})$$

The last step carried out for all grid points yields the combined result

$$\frac{df(s)}{ds} \approx \frac{1}{h} \begin{pmatrix} -1 & 1 & 0 & 0 & \cdots & 0 & 0 \\ 0 & -1 & 1 & 0 & \cdots & 0 & 0 \\ \vdots & & & \ddots & & \vdots & \\ 0 & 0 & 0 & 0 & \cdots & -1 & 1 \\ 0 & 0 & 0 & 0 & \cdots & 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} f(s_1) \\ f(s_2) \\ \vdots \\ f(s_{n-1}) \\ f(s_n) \end{pmatrix} \quad (\text{F.31})$$

As a result, we obtain a matrix representation for the differential operator. Note that the differentiation of $f(s_n)$ at the upper boundary would require an asymptotic correction in order to preserve the overall numerical accuracy.