Comitato Nazionale per L'Energia Nucleare
ISTITUTO NAZIONALE DI FISICA NUCLEARE

Sezione di Pisa
65/3

INFN/BE - 65/4
11 Maggio 1965.

L. Lovitch and S. Rosati : ON THE CORRECTOR FORMULAS FOR THE NUMERICAL SOLUTION OF THE SCHRÖDINGER EQUATION FOR CENTRAL FIELDS. -

Reparto Tipografico
dei Laboratori Nazionali di Frascati

Istituto Nazionale di Fisica Nucleare
Sezione di Pisa

INFN/BE-65/4
11 maggio 1965

L. Lovitch, S. Rosati: ON THE CORRECTOR FORMULAS FOR THE NUMERICAL SOLUTION OF THE SCHRÖDINGER EQUATION FOR CENTRAL FIELDS. -

The evaluation of the eigenvalues and corresponding solutions of a Schrödinger equation is an ever-present problem in atomic and nuclear physics. For the numerical evaluation of the Schrödinger equation for a particle in a central potential, a useful corrector formula was derived by Douglas and Ridley[1] some years ago. Given a first estimate of the eigenvalue, this formula enables one to obtain a better estimate using any standard integration procedure for the differential equation. In a particular example, it was found[1] that it was necessary to start with an initial value which was accurate to about 10% in order that the procedure converge to the desired eigenvalue, and that few iterations were required to obtain the eigenvalue with good precision.

More recently Cooley[2] has obtained a quite similar corrector formula by applying to the problem a general matrix technique developed by Löwdin[3], using the Numerov formula for the numerical integration of the radial Schrödinger equation

$$\frac{d^2y}{dr^2} = \frac{2\mu}{\hbar^2}\left[V(r) - E\right] y = \left[v(r) - \varepsilon\right] y . \tag{1}$$

If we divide the range of integration into equal steps of length h, the Numerov recurrence relation is given by (see ref. [4])

$$z_{i+1} = 2z_i - z_{i-1} + h^2 f_i y_i , \tag{2}$$

where we have written

$$f(r) = v(r) - \varepsilon , \tag{3}$$

and

$$z = \left(1 - \frac{h^2}{12} f\right) y . \tag{4}$$

With reference to the Douglas-Ridley corrector formula, both Hartree[4] and Cooley[2] state that this formula gives first-order convergence in correcting an approximate eigenvalue, that is to say, the true correction differs from the estimated correction by an amount proportional to the latter. If we look at how the Cooley corrector formula has been derived[2], it is clear that it yields quadratic convergence in the correction of the eigenvalue: the eigenvalue is the zero of a certain function and the corrector formula is the Newton-Raphson expression for improving an estimate of the zero of that function.

Here we want to show that the Douglas-Ridley corrector formula has really a quadratic convergence and that the Cooley formula may be derived directly from it.

In solving the Schrödinger equation numerically, for stability reasons it is convenient to perform the integration in two steps: choosing a trial eigenvalue, eq. (1) is integrated outward from the origin and inward from large distances respectively, so as to satisfy the boundary conditions

$$\begin{aligned} y &= 0, \qquad r = 0, \\ y &\to 0, \qquad r \to \infty. \end{aligned} \tag{5}$$

Where the two solutions meet, at r = R say, their logarithmic derivatives are equal if and only if the trial energy value coincides with one of the eigenvalues. And so, the eigenvalues are zeros of the difference of the logarithmic derivatives at r = R, regarded as a function of energy.

Consider the solutions $y(\varepsilon)$, $y(\varepsilon + \delta\varepsilon)$ corresponding to values ε and $\varepsilon + \delta\varepsilon$ of the energy, i. e.

$$y''(\varepsilon) = (v - \varepsilon)\, y(\varepsilon),$$

and (6)

$$y''(\varepsilon + \delta\varepsilon) = (v - \varepsilon - \delta\varepsilon)\, y(\varepsilon + \delta\varepsilon),$$

where the primes denote derivation with respect to the radial coordinate r. It follows that

$$y(\varepsilon)\, y'(\varepsilon + \delta\varepsilon) - y(\varepsilon + \delta\varepsilon)\, y'(\varepsilon) \Big|_{r=a}^{b} = -\delta\varepsilon \int_{r=a}^{b} dr\, y(\varepsilon)\, y(\varepsilon + \delta\varepsilon). \tag{7}$$

Let us "normalise" the outward and inward solutions so that they all pass through the same value y_m at r=R. From eq. (7) we get, at r=R,

$$\frac{y'_{out}(\varepsilon + \delta\varepsilon)}{y_{out}(\varepsilon + \delta\varepsilon)} = \frac{y'_{out}(\varepsilon)}{y_{out}(\varepsilon)} - \frac{\delta\varepsilon}{y_{out}(\varepsilon)\, y_{out}(\varepsilon + \delta\varepsilon)} \int_0^R dr \cdot \tag{8.1}$$

$$\cdot\, y_{out}(\varepsilon)\, y_{out}(\varepsilon + \delta\varepsilon),$$

and

$$\frac{y'_{in}(\varepsilon+\delta\varepsilon)}{y_{in}(\varepsilon+\delta\varepsilon)} = \frac{y'_{in}(\varepsilon)}{y_{in}(\varepsilon)} + \frac{\delta\varepsilon}{y_{in}(\varepsilon)\, y_{in}(\varepsilon+\delta\varepsilon)} \cdot$$

$$\cdot \int_R^\infty dr\, y_{in}(\varepsilon)\, y_{in}(\varepsilon+\delta\varepsilon), \tag{8.2}$$

and so

$$\frac{y'_{out}(\varepsilon+\delta\varepsilon)}{y_{out}(\varepsilon+\delta\varepsilon)} - \frac{y'_{in}(\varepsilon+\delta\varepsilon)}{y_{in}(\varepsilon+\delta\varepsilon)} = \frac{y'_{out}(\varepsilon)}{y_{in}(\varepsilon)} - \frac{y'_{in}(\varepsilon)}{y_{in}(\varepsilon)} -$$

$$- \frac{\delta\varepsilon}{\lfloor \bar{y}_m \rfloor^2} \left\{ \int_o^R dr\, y_{out}(\varepsilon)\, y_{out}(\varepsilon+\delta\varepsilon) + \int_R^\infty dr\, y_{in}(\varepsilon)\, y_{in}(\varepsilon+\delta\varepsilon) \right\} . \tag{9}$$

If ε is a trial eigenvalue, then the required eigenvalue $(\varepsilon+\delta\varepsilon)$ corresponds to the vanishing of the left-hand-side of (9), so that

$$\delta\varepsilon = \frac{\lfloor y'_{out}(\varepsilon) - y'_{in}(\varepsilon) \rfloor\, y_m}{\int_o^R dr\, y_{out}(\varepsilon)\, y_{out}(\varepsilon+\delta\varepsilon) + \int_R^\infty dr\, y_{in}(\varepsilon)\, y_{in}(\varepsilon+\delta\varepsilon)} . \tag{10}$$

This formula is exact and for numerical applications one may approximate it by the expression

$$\delta\varepsilon \simeq \frac{\lfloor y'_{out}(\varepsilon) - y'_{in}(\varepsilon) \rfloor\, y_m}{\int_o^R dr\, \lfloor y_{out}(\varepsilon) \rfloor^2 + \int_R^\infty dr\, \lfloor y_{in}(\varepsilon) \rfloor^2} , \tag{11}$$

which clearly has an error $0\lfloor (\delta\varepsilon)^2 \rfloor$. The expression (11) coincides with the Douglas-Ridley corrector formula, which has therefore quadratic convergence.

The deduction of the Cooley corrector formula from (11) is quite straightforward. Taking two points symmetrically situated at a distance h from the point r=R, we have

$$y_{out,\,m-1} = \sum_{k=0}^{\infty} \frac{(-h)^k}{k!}\, y^{(k)}_{out,\,m} , \tag{12.1}$$

and

$$y_{in,\,m+1} = \sum_{k=0}^{\infty} \frac{h^k}{k!}\, y^{(k)}_{in,\,m} . \tag{12.2}$$

Since $y_{m,\,in} = y_{m,\,out} = y_m$ and $y^{(2)}_{m,\,in} = y^{(2)}_{m,\,out}$ (the latter is a consequence

of the Schrödinger equation), it follows that

$$y'_{out,m} - y'_{in,m} = h^{-1}\left[-y_{out,m-1} - y_{in,m+1} + 2y_m + h^2 y_m^{(2)} - \right.$$
$$\left. - \frac{h^3}{6} y^{(3)}_{out,m} + \frac{h^3}{6} y^{(3)}_{in,m} + \frac{h^4}{24} y^{(4)}_{out,m} + \frac{h^4}{24} y^{(4)}_{in,m} + 0(h^5) \right]. \tag{13}$$

Using eq. (4) and

$$y^{(3)} = f' y + f y' , \tag{14}$$

it follows that

$$y'_{out,m} - y'_{in,m} = h^{-1}\left[-z_{out,m-1} - z_{in,m+1} + 2z_m + h^2 f_m y_m - \right.$$
$$\left. - \frac{h^3}{12} f_m (y'_{out,m} - y'_{in,m}) + 0(h^5) \right],$$

hence

$$(1 + \frac{h^2}{12} f_m)(y'_{out,m} - y'_{in,m}) = h^{-1}\left[-z_{out,m-1} - z_{in,m+1} + 2z_m + \right.$$
$$\left. + h^2 f_m y_m \right] + 0(h^4). \tag{15}$$

Eq. (11) therefore becomes

$$\delta\varepsilon \simeq \frac{h^{-1} y_m \left[-z_{out,m-1} - z_{in,m+1} + 2z_m + h^2 f_m y_m \right]}{(1 + \frac{h^2}{12} f_m)\left\{ \int_0^R dr\, y^2_{out} + \int_R^\infty dr\, y^2_{in} \right\}} + 0(h^4)$$

$$= \frac{h^{-1} z_m \left[-z_{out,m-1} - z_{in,m+1} + 2z_m + h^2 f_m y_m \right]}{\int_0^R dr\, y^2_{out} + \int_R^\infty dr\, y^2_{in}} + 0(h^4) . \tag{16}$$

The Cooley corrector formula is given by the latter expression with the integrals of the denominator approximated by the simple trapezoidal integration formula.

An extension of the preceding method in the research of the potential of a given analytic form which best reproduces a set of experimental data is in progress.

REFERENCES

(1) - E. C. Ridley, Proc. Cambridge Phil. Soc. 51, 702 (1952).
(2) - J. W. Cooley, Math. Comp. 15, 363 (1961).
(3) - P. O. Löwdin, "An Elementary Interation-Variation Method for Solving the Schrödinger Equation", Technical Note from the Uppsala Chemistry Group, 1958; J. Mol. Spectroscopy 10, 12 (1963).
(4) - D. R. Hartree, The Calculation of Atomic Structures (Wiley, New York, 1957).

^^^^^^^^^^^^^^^^^