Theory of the Shooting Method for the Radial Schrödinger Equation: Hydrogen Atom Case Study

1 Introduction

The hydrogen atom is a cornerstone problem in quantum mechanics, with analytic solutions that form the basis for understanding atomic structure. However, its numerical solution using techniques such as the **shooting method** provides essential practice in computational physics and boundary value problems. This lesson explains in detail the physical principles, mathematical structure, and algorithmic realization of the shooting method for solving the radial Schrödinger equation, including the rationale for using the Runge-Kutta method as a robust numerical integrator.

2 The Radial Schrödinger Equation

The time-independent Schrödinger equation for a particle of mass m in a spherically symmetric potential $V(r)$ is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\Psi(\vec{r}) = E\Psi(\vec{r}), \tag{1}$$

where for the hydrogen atom, $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$.

By separation of variables, we write

$$\Psi(\vec{r}) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi). \tag{2}$$

The radial function satisfies

$$-\frac{\hbar^2}{2m}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} - \frac{\ell(\ell+1)}{r^2}R\right] + V(r)R = ER, \tag{3}$$

or, equivalently, by defining $u(r) = rR(r)$,

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right]u = Eu. \tag{4}$$

3 Boundary Conditions and Physical Solutions

Physically acceptable solutions must:

1. Be finite at $r = 0$: for $\ell = 0$, $u(0) = 0$; for $\ell > 0$, $u(r) \sim r^{\ell+1}$.
2. Decay to zero as $r \to \infty$ (normalizability).

These requirements make the Schrödinger equation a two-point boundary value problem (BVP).

4 The Shooting Method: Concept and Implementation

The shooting method converts the BVP into an initial value problem (IVP) [**?**]. One:

- Chooses a trial energy E.
- Integrates the equation outward from $r_{\min}$ (close to zero) to a large $r_{\max}$ using given initial conditions, e.g. $u(r_{\min}) \approx 0$, $u'(r_{\min}) = 1$.
- Checks whether the integrated wavefunction at $r_{\max}$ satisfies the boundary condition ($u(r_{\max}) \to 0$).
- Adjusts E (using a root-finding or stepping scheme) until $u(r_{\max})$ is sufficiently close to zero, indicating an eigenvalue.

This process exploits the fact that only for discrete energies (eigenvalues) do the solutions remain bounded and normalizable.

5 Runge-Kutta Method for Integration

The second-order ODE in Eq. (4) is rewritten as a first-order system:

$$\begin{cases} u_1 = u \\ u_2 = \frac{du}{dr} \end{cases}$$

so that

$$\frac{du_1}{dr} = u_2, \qquad \frac{du_2}{dr} = \left[\frac{\ell(\ell+1)}{r^2} - \frac{2m}{\hbar^2}(V(r) - E)\right] u_1.$$

To numerically solve this system, the **fourth-order Runge-Kutta method** (RK4) is widely used due to its high stability and accuracy for smooth ODEs [**?**]. For each integration step, the RK4 method computes intermediate "slopes" and takes a weighted average to advance the solution, which is essential for avoiding numerical divergence in quantum mechanical problems (see also [**?**, **?**]).

6 Algorithmic Steps of the Shooting Method

1. **Set physical constants and discretization:** Choose $r_{\min}$, $r_{\max}$, and step size h; initialize arrays for u and du/dr.
2. **For a given trial energy E, integrate the system using RK4:** Propagate from $r_{\min}$ to $r_{\max}$, storing u at each point.
3. **Monitor the wavefunction:** If $u(r_{\max})$ is close to zero (within a defined tolerance), accept E as an eigenvalue.
4. **If not, adjust E and repeat:** Use a root-finding approach (bisection, Newton-Raphson, or secant) to search for energies where $u(r_{\max})$ crosses zero.
5. **Repeat for desired quantum numbers.**

7 Physical Interpretation and Practical Considerations

- The shooting method physically mimics "shooting" a solution from the origin and seeing whether it "lands" at the desired boundary (zero at infinity). - For each allowed quantum number n, only specific discrete energy values yield solutions satisfying both boundary conditions; these are the quantized bound state energies. - The method is sensitive to step size and initial conditions; very poor choices may cause the solution to diverge or miss eigenvalues. - Wavefunction normalization is not crucial during energy search; physical normalization is performed once the eigenfunction and eigenvalue are found.

8 Numerical Instabilities and Remedies

- If the energy guess is far from an eigenvalue, the wavefunction can blow up (exponential growth) or oscillate rapidly, causing overflows.
- Normalizing the wavefunction during propagation can sometimes help, but the sign and relative zero crossing are the main indicators for convergence.
- Adaptive step size integrators and double-precision arithmetic improve robustness.
- Checking for overflow and implementing early stopping prevents wasted computation.

9 References and Further Reading

1. A. L. Garcia, *Numerical Methods for Physics*, 2nd Ed., Prentice Hall, 2000.
2. R. H. Landau, M. J. Paez, C. C. Bordeianu, *Computational Physics: Problem Solving with Computers*, 3rd Ed., Wiley-VCH, 2015.

3. A. J. Goldberg, H. M. Schey, J. L. Schwartz, "Computer-generated motion pictures of one-dimensional quantum-mechanical transmission and reflection phenomena," *Am. J. Phys.* **35**, 177 (1967).

4. R. Shankar, *Principles of Quantum Mechanics*, 2nd Ed., Springer, 1994.

5. Wikipedia contributors, "Shooting method," `https://en.wikipedia.org/wiki/Shooting_method`