Numerical solutions of Schrödinger's equation applied to atomic physics

Lucas Madeira [1]

Lecture 3
School on Light and Cold Atoms

IFSC UNIVERSITY OF SÃO PAULO
São Carlos Institute of Physics

March 16, 2023

[1] madeira@ifsc.usp.br

Program

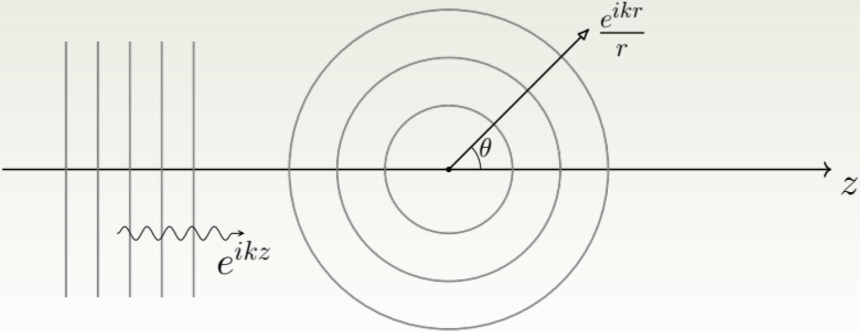
- March 14 - Lecture 1 - The shooting method (1/2)
  - Strategy
  - Units
  - Numerical differentiation and integration
  - Infinite square well
- March 15 - Lecture 2 - The shooting method (2/2)
  - Code development
  - Q&A
- March 16 - Lecture 3 - Low-energy scattering (1/2)
  - Phase shifts
  - Scattering length
  - Spherical well
- March 17 - Lecture 4 - Low-energy scattering (2/2)
  - Code development
  - Q&A

References

- Mathias M. Lima and Lucas Madeira, **Scattering length and effective range of microscopic two-body potentials**, arXiv:2303.04591, `https://arxiv.org/abs/2303.04591`
- Quantum mechanics textbooks that cover scattering: Griffiths, Sakurai, ...

Scattering theory

- A particle, initially far away from the region where it will be scattered, moving toward the scattering center $\rightarrow$ initial state is a plane-wave
- The final state is the result of the action of a scattering potential on the particle $\rightarrow$ at large distances it is an outgoing spherical wave
- The potential has a finite range



Partial waves expansion

- $V(\mathbf{r})$ is finite-ranged
- One more restriction: that it is spherically symmetric, $V(\mathbf{r}) = V(r)$

$$\psi_{\mathbf{k}}(r,\theta) \xrightarrow{\text{large } r} \mathcal{N}\left[e^{ikz} + \frac{e^{ikr}}{r} f(\theta)\right]$$

- In the scattering region $(0 < r < R)$:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

- $E = \hbar^2 k^2 / 2m$
- We propose a separable solution of the form:

$$\psi(r,\theta,\phi) = A_l(r) Y_l^m(\theta,\phi)$$

- ∇^2 in spherical coordinates
- We perform a change of variables $A_l(r) = u_l(r)/r$

Partial waves expansion

- Reduced radial wave function
$$\left(\frac{d^2}{dr^2}+k^2-\frac{2mV(r)}{\hbar^2}-\frac{l(l+1)}{r^2}\right)u_l(r)=0$$
- At the origin, $A_l(r)=u_l(r)/r$ is finite $\rightarrow u_l(0)=0$
- Outside ($r>R$), the solution is of the form:
$$u_l(r)=c_l' r j_l(kr)+c_l'' r n_l(kr)$$

Partial waves expansion

- Free particle (plane-wave)

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta)$$

- Asymptotic behavior

$$e^{ikr\cos\theta} \xrightarrow{\text{large } r} \sum_{l=0}^{\infty} \frac{(2l+1)}{2ikr} \left[e^{ikr} - (-1)^l e^{-ikr}\right] P_l(\cos\theta)$$

- Motivated by this, we write the solution for every $r > R$ as

$$\psi(r,\theta) = \mathcal{N} \sum_{l=0}^{\infty} i^l (2l+1) \frac{u_l(r)}{r} P_l(\cos\theta)$$

- Asymptotic behavior

$$\psi(r,\theta) \xrightarrow{\text{large } r} \mathcal{N} \sum_{l=0}^{\infty} \frac{(2l+1)}{ikr} \left[c_l^{(1)} e^{ikr} - (-1)^l c_l^{(2)} e^{-ikr}\right] P_l(\cos\theta)$$

Partial waves expansion

- Compare both asymptotic behaviors

$$e^{ikr\cos\theta} \xrightarrow{\text{large } r} \sum_{l=0}^{\infty} \frac{(2l+1)}{2ikr} \left[e^{ikr} - (-1)^l e^{-ikr}\right] P_l(\cos\theta)$$

$$\psi(r,\theta) \xrightarrow{\text{large } r} \mathcal{N} \sum_{l=0}^{\infty} \frac{(2l+1)}{ikr} \left[c_l^{(1)} e^{ikr} - (-1)^l c_l^{(2)} e^{-ikr}\right] P_l(\cos\theta)$$

- If $c_l^{(1)} = c_l^{(2)} = 1/2$, then both equations are the same
- Not surprising since this particular choice makes the radial function the same as the one for a free particle
- If $c_l^{(1)} \neq c_l^{(2)}$, then scattering certainly took place
- Ratio of the two coefficients: the proportion of outgoing to incoming spherical waves
- Quantify the impact of the scattering potential on the free particle

Phase shifts

- Introduce a new quantity:

$$\frac{c_l^{(1)}}{c_l^{(2)}} = e^{2i\delta_l(k)}$$

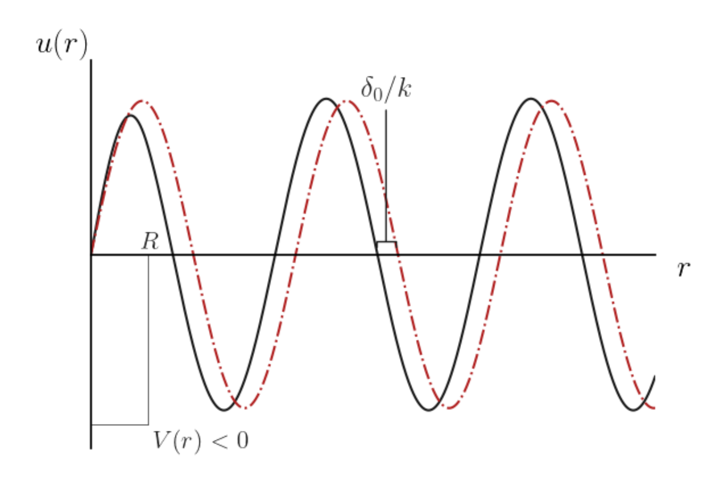
- $\delta_l(k)$ are called phase shifts
- Now we can attribute physical meaning to the partial wave scattering amplitude and the phase shifts
- Conservation of the probability during scattering tells us that, at large distances, the only thing that can change is the phase of the wave function (with respect to the incident wave)
- The difference between the phases is the phase shift $\delta_l(k)$

Phase shifts

- When there is no scattering, $V = 0$ and $\delta_l(k) = 0$
- For a potential $V \neq 0$, the radial solution for $r < R$ will depend on the details of the potential
- However, we have a free particle solution outside the range R of the potential, $V(r > R) = 0$
- Hence, what happens inside the range of the potential determines the phase shift observed outside of it
- The advantage of this formulation $\rightarrow$ whole process in terms of a real quantity $\delta_l(k)$

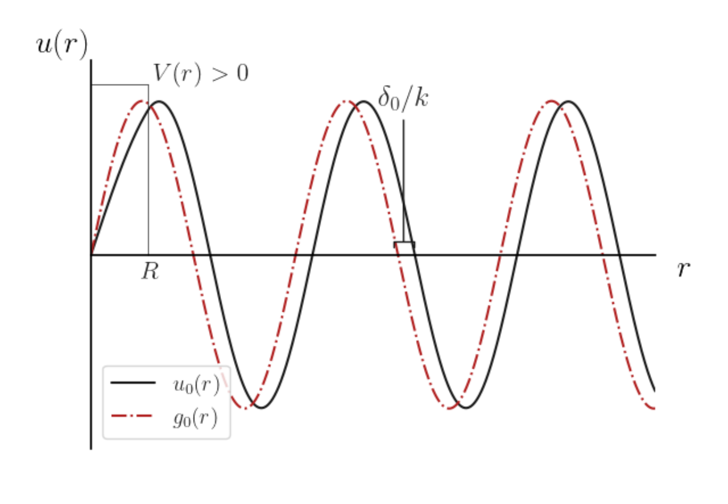
Phase shifts

- Attractive potential: $\delta_0(k) > 0$



Phase shifts

- Repulsive potential: $\delta_0(k) < 0$



The low-energy limit and the scattering length

- Reduced radial equation for the l-th partial wave

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - E\right) u_l(r) = 0$$

- Effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

- Low-energy ($E \approx 0$): particle cannot overcome the barrier
- $l = 0$: there is no barrier $\rightarrow$ s-wave

$$A_0(r) = \frac{u_0(r)}{r} \quad = \quad e^{i\delta_0}(\cos\delta_0 j_0(kr) - \sin\delta_0 n_0(kr)) = e^{i\delta_0}\left[\frac{1}{kr}\sin(kr+\delta_0)\right]$$

The low-energy limit and the scattering length

- Schrödinger's equation for the radial solution becomes very simple in this situation
- Outside the range of the potential, $V(r > R) = 0$
- There is no centrifugal barrier since $l = 0$
- Low-energy scattering: $k \approx 0$

$$u_0''(r) = 0$$

- The solution is a line:

$$u_0(r) = c(r - a)$$

- Logarithmic derivative $\left(\frac{d}{dx}\ln f(x) = \frac{f'(x)}{f(x)}\right)$:

$$\frac{u_0'(r)}{u_0(r)} = \frac{1}{r - a}$$

- Match the logarithmic derivative of $e^{i\delta_0}\left[\frac{1}{k}\sin(kr + \delta_0)\right]$

The low-energy limit and the scattering length

$$k \cot(kr + \delta_0) = \frac{1}{r - a}$$

- In the limit $k \to 0$, and $r = 0$

$$\boxed{\lim_{k \to 0} k \cot \delta_0(k) = -\frac{1}{a}}$$

Summary

- Previously, we reduced the scattering problem to computing the phase shifts $\delta_l(k)$
- Low-energy phenomena: $l = 0$ dominates
- In the zero-energy limit a single number encodes all the information we need about scattering

The scattering length

- As its name suggests: dimension of length
- It may differ by orders of magnitude from the range R of the potential
- Geometrical interpretation:

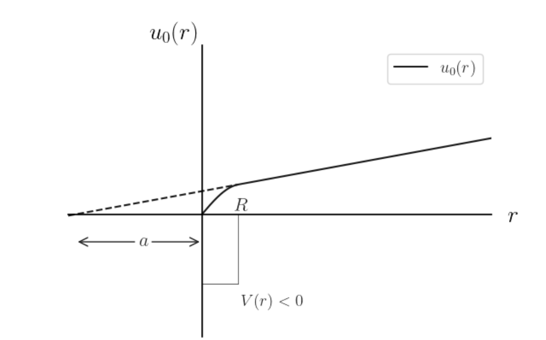
$$u_0(r > R) = 1 - \frac{r}{a}$$

- Intercept of the outside wave function

The scattering length

$$u_0(r > R) = 1 - \frac{r}{a}$$

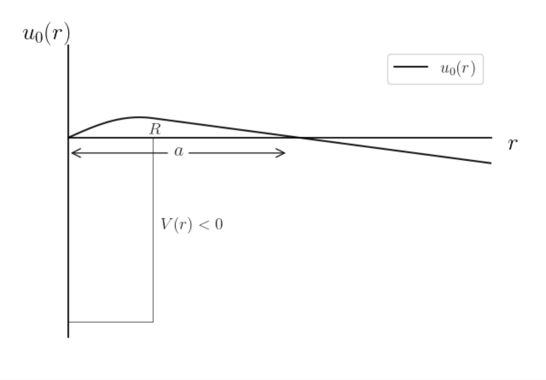
- An attractive potential that is not strong enough to produce a bound state
- $a < 0$ because we need to extrapolate the radial function to negative values to intercept the r-axis



The scattering length

$$u_0(r > R) = 1 - \frac{r}{a}$$

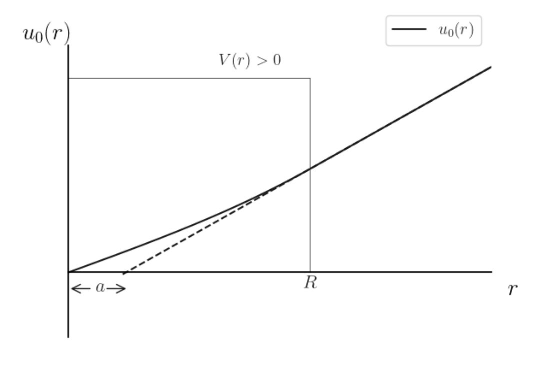
- A stronger attractive potential produces a bound state
- $a > 0$



The scattering length

$$u_0(r > R) = 1 - \frac{r}{a}$$

- For a repulsive potential, we always have $a > 0$



Two-body scattering

- So far, we considered only a single particle being scattered by a finite-ranged potential $V(r)$ located at $r = 0$
- With a few modifications: two particles interacting through a pairwise potential $V(r)$

$$H = -\frac{\hbar^2}{2m_1}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m_2}\nabla^2_{\mathbf{r}_2} + V(\mathbf{r}_1 - \mathbf{r}_2)$$

- We define the coordinates:

$$\begin{aligned} \mathbf{R} &= \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M} \\ \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \end{aligned}$$

- $M = m_1 + m_2$
- $H = H_{\text{CM}} + H_r$

$$H_{\text{CM}} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} \qquad \text{and} \qquad \boxed{H_r = -\frac{\hbar^2}{2m_r}\nabla^2_{\mathbf{r}} + V(r)}$$

- $m_r = m_1 m_2/(m_1 + m_2)$ is the reduced mass

Spherically symmetric finite well

- Analytical results

$$V(r) = \begin{cases} -v_0 \dfrac{\hbar^2}{m_r R^2}, & \text{for } r < R, \\ 0, & \text{for } r > R \end{cases}$$

- $v_0 > 0$ is a dimensionless parameter related to the depth of the well
- For a relatively shallow or short-ranged potential, we may only observe continuum scattering states: $E > 0$
- Increasing its depth or range may make it strong enough to produce a bound state: $E < 0$
- Let us start with the $E > 0$ case
- We need to solve the s-wave ($l = 0$) equation:

$$\left(\frac{d^2}{dr^2} - \frac{2m_r}{\hbar^2} V(r) + \frac{2m_r}{\hbar^2} E \right) u(r) = 0$$

Spherically symmetric finite well

- Explicitly:

$$u''(r) + \left(k_0^2 + k^2\right) u(r) = 0 \qquad \text{for } r < R,$$
$$u''(r) + k^2 u(r) = 0 \qquad \text{for } r > R$$

- $k^2 \equiv 2m_r E/\hbar^2$ and $k_0^2 \equiv 2v_0/R^2$
- In the region $r < R$, the solution may be written as:

$$u(r) = A \sin\left(\sqrt{k^2 + k_0^2}\, r\right) + B \cos\left(\sqrt{k^2 + k_0^2}\, r\right)$$

- $A(r) = u(r)/r \to u(0) = 0 \to B = 0$

Spherically symmetric finite well

$$u(r) = \begin{cases} A \sin\left(\sqrt{k^2 + k_0^2}\, r\right) & \text{for } r < R, \\ \cot \delta_0(k) \sin(kr) + \cos(kr) & \text{for } r > R \end{cases}$$

- The logarithmic derivatives must be equal

$$\left[\frac{u'(r)}{u(r)}\right]_{r=R^-} = \left[\frac{u'(r)}{u(r)}\right]_{r=R^+}$$

$$\frac{\sqrt{k^2 + k_0^2} \cos\left(\sqrt{k^2 + k_0^2}\, R\right)}{\sin\left(\sqrt{k^2 + k_0^2}\, R\right)} = \frac{k \cot \delta_0(k) \cos(kR) - k \sin(kR)}{\cot \delta_0(k) \sin(kR) + \cos(kR)}$$

- After some manipulations:

$$\delta_0(k) = -kR + \arctan\left[\frac{k \tan\left(\sqrt{k^2 + k_0^2}\, R\right)}{\sqrt{k^2 + k_0^2}}\right]$$

Spherically symmetric finite well

- To calculate the scattering length a, we need to take the $k \to 0$ limit

$$\lim_{k \to 0} k \cot \delta_0(k) = -\frac{1}{a} + \mathcal{O}(k^2)$$

$$\frac{\sqrt{k^2 + k_0^2} \cos\left(\sqrt{k^2 + k_0^2}\, R\right)}{\sin\left(\sqrt{k^2 + k_0^2}\, R\right)} = \frac{k \cot \delta_0(k) \cos(kR) - k \sin(kR)}{\cot \delta_0(k) \sin(kR) + \cos(kR)}$$

- Rearrange the equation so that we have factors of $k \cot \delta_0(k)$
- $\cos(kR) = 1 + \mathcal{O}(k^2)$
- $\sin(kR) = kR + \mathcal{O}(k^3)$
- The result is:

$$\sqrt{k_0^2} \cot\left(\sqrt{k_0^2}\, R\right) = \frac{-1/a}{-R/a + 1}$$

Spherically symmetric finite well

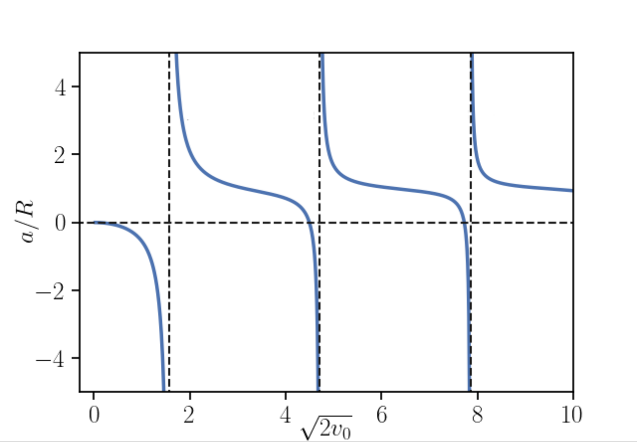
- Solving for the scattering length:

$$\boxed{a = R - \frac{\tan\left(\sqrt{k_0^2}R\right)}{\sqrt{k_0^2}} = R\left(1 - \frac{\tan\left(\sqrt{2v_0}\right)}{\sqrt{2v_0}}\right)}$$

- $k_0^2 = 2v_0/R^2$

Spherically symmetric finite well

$$\boxed{a = R\left(1 - \frac{\tan\left(\sqrt{2v_0}\right)}{\sqrt{2v_0}}\right)}$$



Spherically symmetric finite well

- Bound states: $E < 0$
- Repeat the same procedure or $\boxed{k = i\kappa} \to E = \hbar^2 k^2/2m_r = -\hbar^2\kappa^2/2m_r$

$$u(r) = \begin{cases} A' \sin\left(\sqrt{k_0^2 - \kappa^2}\, r\right) & \text{for } r < R, \\ B' e^{-\kappa r} & \text{for } r > R \end{cases}$$

- Match the logarithmic derivative

$$\left[\frac{u'(r)}{u(r)}\right]_{r=R^-} = \left[\frac{u'(r)}{u(r)}\right]_{r=R^+}$$

$$\frac{\sqrt{k_0^2 - \kappa^2}\cos\left(\sqrt{k_0^2 - \kappa^2}\, R\right)}{\sin\left(\sqrt{k_0^2 - \kappa^2}\, R\right)} = \frac{-\kappa e^{-\kappa R}}{e^{-\kappa R}}$$

Spherically symmetric finite well

- After some manipulations:

$$\tan\left(\sqrt{k_0^2 - \kappa^2}\, R\right) + \frac{\sqrt{k_0^2 - \kappa^2}}{\kappa} = 0$$

- Transcendental equation for the bound-state energies
- $\sqrt{k_0^2 - \kappa^2}/\kappa$ is always positive
- Then $\tan\left(\sqrt{k_0^2 - \kappa^2}\, R\right)$ must be negative if we want the equation to have solution(s)

$$\frac{\pi}{2} + n\pi < \sqrt{k_0^2 - \kappa^2}\, R < \pi + n\pi$$

- n is an integer
- $\sqrt{k_0^2 - \kappa^2}\, R$ is always positive $\rightarrow n = 0, 1, \ldots$
- The first bound state is $n = 0$

Spherically symmetric finite well

- The first bound state is $n = 0$

$$\frac{\pi}{2R} < \sqrt{k_0^2 - \kappa^2} < \frac{\pi}{R}$$

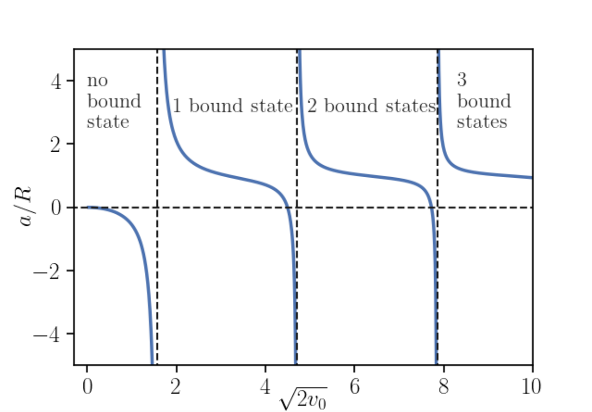
- $k_0 > \sqrt{k_0^2 - \kappa^2}$
- $k_0 = \sqrt{2v_0}/R$

$$\boxed{v_0 > \frac{\pi^2}{8}}$$

- There are no bound states if v_0 is not above a certain threshold value

$$\boxed{a = R\left(1 - \frac{\tan\left(\sqrt{2v_0}\right)}{\sqrt{2v_0}}\right)}$$

- $\sqrt{2v_0} = \pi/2 + n\pi$ $(n = 0, 1, 2, ...)$ $\rightarrow$ a diverges $\rightarrow$ potential admits an additional bound state



Summary

- Schrödinger's equation + spherically symmetric potential $V(r)$
- Separable solution $\rightarrow$ radial equation for $A_l(r)$
- Change of variables: $A_l(r) = u_l(r)/r$

$$\left(\frac{d^2}{dr^2} + k^2 - \frac{2m_r V(r)}{\hbar^2} - \frac{l(l+1)}{r^2}\right) u_l(r) = 0$$

- Boundary condition: $A_l(r) = u_l(r)/r \rightarrow u_l(0) = 0$
- Low-energy scattering
  - s-wave: $l = 0$
  - $k \rightarrow 0$

$$\boxed{\frac{d^2 u(r)}{dr^2} - \frac{2m_r V(r)}{\hbar^2} u(r) = 0}$$

- For $r > R$: $V(r > R) = 0$

Numerical procedure

- We want to compute the scattering length numerically
- We need the reduced radial wave function $u(r)$ inside the range of the potential

$$\boxed{\frac{d^2u(r)}{dr^2} - \frac{2m_r V(r)}{\hbar^2} u(r) = 0}$$

- We can use the discretization procedure that we saw in the first lecture
  - $E = 0$: we do not have to determine the energy

Review

- First lecture
- Taylor series:

$$
\begin{aligned}
u(r+\Delta r) &= u(r) + (\Delta r)u'(r) + \frac{(\Delta r)^2}{2}u''(r) + \frac{(\Delta r)^3}{6}u'''(r) + \cdots \\
u(r-\Delta r) &= u(r) - (\Delta r)u'(r) + \frac{(\Delta r)^2}{2}u''(r) - \frac{(\Delta r)^3}{6}u'''(r) + \cdots
\end{aligned}
$$

- Their difference/sum:

$$
\begin{aligned}
\left.\frac{du}{dr}\right|_{r=r_i} &\approx \frac{u_{i+1} - u_{i-1}}{2\Delta r} \\
\left.\frac{d^2u}{dr^2}\right|_{r=r_i} &\approx \frac{u_{i+1} - 2u_i + u_{i-1}}{(\Delta r)^2}
\end{aligned}
$$

Numerical procedure

$$\frac{d^2u(r)}{dr^2} - \frac{2m_r V(r)}{\hbar^2} u(r) = 0$$

- Discretization:

$$u_{i+1} = 2u_i - u_{i-1} + \frac{2m_r(\Delta r)^2}{\hbar^2} V(r_i) u_i$$

- We need two consecutive points to start the algorithm
  - $u(0) = 0 \rightarrow u_0 = 0$
  - $u(\Delta r) =$[some non-zero value] $\rightarrow u_1 = 1$
- It is convenient to use dimensionless quantities

Numerical procedure

Find the reduced wave function inside the range of the potential

- Inputs
  - Number of points N or their spacing Δr
  - Parameters of the potential: v_0 and R

1. Set $u_0 = 0$, $u_1 = 1$, and $i = 1$
2. Compute u_{i+1}:
   - $u_{i+1} = 2u_i - u_{i-1} + \frac{2m_r(\Delta r)^2}{\hbar^2} V(r_i) u_i$
3. If $r_i \geqslant R + \Delta r$, stop. Else, increment i by one
4. Go to step 2

Scattering length

- Outside the range of the potential and $k \to 0$

$$g_0(r > R) = 1 - \frac{r}{a}$$

- Logarithmic derivative:

$$\frac{g_0'(r)}{g_0(r)} = \frac{1}{r-a} \qquad \text{for } r > R$$

- Match with your numerical solution at $r = R$

$$u'_{\mathrm{num}}(R) = \left.\frac{du(r)}{dr}\right|_{r=R} = \frac{u(R+\Delta r) - u(R-\Delta r)}{2\Delta r}$$

- Expression that relates the numerical solution and the scattering length:

$$\boxed{a = R - \frac{2\Delta r\, u(R)}{u(R+\Delta r) - u(R-\Delta r)}}$$

Project

Write a program that finds the solution to the zero-energy s-wave Schrödinger's equation for two particles interacting through an attractive spherical well. The depth and range of the well are inputs

- Find the reduced radial wave function
- Use it to calculate the scattering length
- Fix the range of the potential $R = 1$ (in our dimensionless units)
  - Find v_0 such that $a = \pm 1, \pm 10$ and $|a| \to \infty$
  - Compare your results with the analytical expression:

$$a = R\left(1 - \frac{\tan\left(\sqrt{2v_0}\right)}{\sqrt{2v_0}}\right)$$

- Plot $u(r)$ for 3 cases: $a < 0$, $|a| \to \infty$, and $a > 0$. What is the difference between them?
- What are examples of other potentials that can be solved with this method?

- Answer with 3 decimal places (you may need more!)

a/R	v_0
-1	0.679
-10	1.141
$\pm\infty$	$\pi^2/8$
10	1.342
1	$\pi^2/2$