Numerov-Cooley Method : 1-D Schr. Eq.

Last time: Rydberg, Klein, Rees Method and Long-Range Model

G(v), B(v) rotation-vibration constants

↓

$V_J(x)$ potential energy curve

↓ $x = R - R_e$

$E_{v,J}, \psi_{v,J}$, all conceivable experiments including wavepackets, $wp(x,t)$

$$wp(x,t) = \sum_i a_i \psi_i e^{-E_i t/\hbar}$$

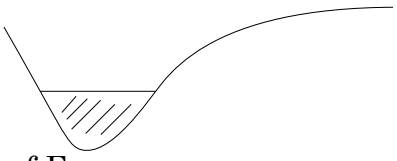
Treated in Lectures #19 and #20

a_i: Initial preparation of wp: $a_i = \int \psi_i^* \left[wp(x,0) \right] dx$

$e^{-E_i t/\hbar}$: determined by $V_J(x)$ free evolution of wp

Completeness: Any arbitrary wavefunction may be expanded as a linear combination of *eigenstates* of **H**.

Method for RKR derivation: A(E,J) = area of V(x) below E:



used WKB Quantization Condition

obtained $x_\pm(E,J)$ − a series of pairs of turning points on a grid of E.

Today: What do we do when we have a potential energy curve, $V_J(x)$, (especially when V(x) is not suited for WKB)?

Solve Schr. Eq. numerically!

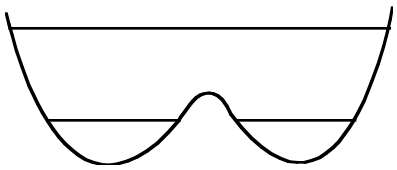
- No models
- 15 digit reproducibility
- cheap

This is the final tool we will develop for use in the Schrödinger representation. To summarize the classes of 1–D problem we are able to solve:

* piecewise constant potentials (matrix approach for joining at $\psi(x)$ boundaries)
* Airy functions (linear potential and joining JWKB across turning point) **[Not done in 2018]**
* JWKB (quantization condition and semi-classical wavefunctions)
* numerical integration (today)

See Merzbacher Quantum Mechanics pp. 92-103

Numerical Integration of the 1-D Schrödinger Equation



widely used
incredibly accurate
no restrictions on V(x) or on E–V(x) [e.g. nonclassical region, near turning points, double minimum potential, kinks in V(x).]
For most 1-D problems, where all one cares about is a set of $\{E_i, \psi_i\}$, where ψ_i is defined on a grid of points x_i, one uses Numerov-Cooley

leroy.uwaterloo.ca/programs.html

LEVEL: A computer program for solving the radial Schrödinger equation for bound and quasibound levels
R.J. Le Roy, *Journal of Quantitative Spectroscopy and Radiative Transfer* **186**, 167-178 (2016).
RKR1 – A Computer Program implementing the first-order RKR method for determining diatomic molecule potential energy functions
R.J. Le Roy, *Journal of Quantitative Spectroscopy and Radiative Transfer* **186**, 158-166 (2016).

J. A.Tellinghuisen, "Potential Fitting RKR Method: Semiclassical vs. Quantal Comparisons". *Journal of Molecular Spectroscopy***. 330**, 20-27 (2016).

Supplements for Lecture #9:

1. Cooley, Math. Comput. 15, 363 (1961).
2. Press et. al., Numerical Recipes, Chapters 16 and 17
3. Classic unpublished paper by Zare and Cashion with listing of Fortran program [now better to see LeRoy web site]
4. Tests of Numerov-Cooley vs. other methods by Tellinghuisen
5. LeRoy JQSRT paper

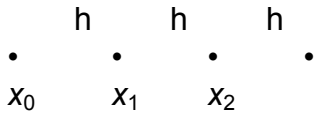
Basic Idea: grid method

* solve differential equation by starting at some x_i and propagating trial solution from one grid point to the next

* apply $\Psi(x) = 0$ boundary conditions at $x = 0$ and ∞ by two different tricks and then force agreement between $\psi_{left}(x)$ and $\psi_{right}(x)$ at some intermediate point by adjusting E.

Euler's Method

want $\psi(x)$ at a series of grid points $x_0, x_1, \ldots x_n = x_0 + nh$



call these $\psi_i = \psi(x_i)$

Need a "generating function," $f(x_n, \psi_n)$

$$\psi_{n+1} = \psi_n + h f(x_n, \psi_n)$$

prescription for going $n \rightarrow n+1$ must depend on both x_n and ψ_n. x_n samples potential, ψ_n samples previous value of ψ.

h ↑ increment in x

$x_{n+1} - x_n = h$ [NOT Planck's constant]

(ψ_n is a number, not the entire wavefunction.)
For the Euler method, the generating function is simply:

$$f(x_n, \psi_n) = \left.\frac{d\psi}{dx}\right|_{x_n} \approx \frac{\psi_{n+1} - \psi_n}{x_{n+1} - x_n} = \frac{\psi_{n+1} - \psi_n}{h}$$

The value of this derivative actually comes from the differential equation that ψ must satisfy, not from prior knowledge of $\psi(x)$ (which we do not yet have!)

For the Schrödinger Eqn. $\frac{d^2\psi}{dx^2} = -\frac{2\mu}{\hbar^2}(E - U(x))\psi$

All constants absorbed in V(x). V(x) must be in units of Å^{-2}.

note that $V(x) = -k(x)^2 = \frac{-p(x)^2}{\hbar^2}$

$$\frac{d^2\psi}{dx^2} = V(x)\psi(x)$$

$V(x) \equiv C[U(x) - E]$ $U(x)$ is the potential.

$C = 10^{-16}\left(8\pi^2 c\mu/h\right)$ h here is *not* increment of distance, — Planck

$= 0.0593203146\mu_A$ h and x are in Å. E and $U(x)$ are in

$$\left.\frac{d\psi}{dx}\right|_{x_i} \equiv \frac{\psi_{i+1} - \psi_i}{h}$$ — not Planck

$\left(\mu_A \text{ in } amu = \frac{\text{gram}}{mole}, {}^{12}C\right)$ cm^{-1} units (E/hc)

$$\left.\frac{d^2\psi}{dx^2}\right|_{x_i} = \left\{\left[\frac{\psi_{i+1} - \psi_i}{h}\right] - \left[\frac{\psi_i - \psi_{i-1}}{h}\right]\right\} \Big/ h$$

$$= h^{-2}\left[\psi_{i+1} - 2\psi_i + \psi_{i-1}\right]$$

$\mu_A = \frac{m_1 m_2}{m_1 + m_2}$

(Planck's constant h is in italics, grid spacing h is not italic.)

Schr. Eq. tells us the rule for propagating ψ. Employing Euler's method (h is not Planck's constant):

$$h^{-2}\left[\psi_{i+1} - 2\psi_i + \psi_{i-1}\right] = V_i\psi_i$$ rearrange to solve for ψ_{i+1}

$$\psi_{i+1} - 2\psi_i + \psi_{i-1} = h^2 V_i \psi_i$$

$$\psi_{i+1} = 2\psi_i - \psi_{i-1} + h^2 V_i \psi_i$$ a recursion relationship. Need *both* ψ_i and ψ_{i-1} to get ψ_{i+1}.

In order to *get things started* we need two values of ψ starting at either edge of the region where ψ is defined and ψ starts out very small.

[See Press et. al. handout (Numerical Recipes, Chapters 16 and 17) for discussion of nth-order Runge-Kutta method. The **generator** is chosen more cleverly than in the Euler method so that stepping errors are minimized by taking more derivatives at intermediate points in the x_i, x_{i+1} interval.]

Cooley specifies

$$y_{i+1} = 2y_i - y_{i-1} + h^2 V_i \psi_i$$

$$y_i = \left[1 - \left(h^2/12\right)V_i\right]\psi_i \text{ (and vice versa)}$$

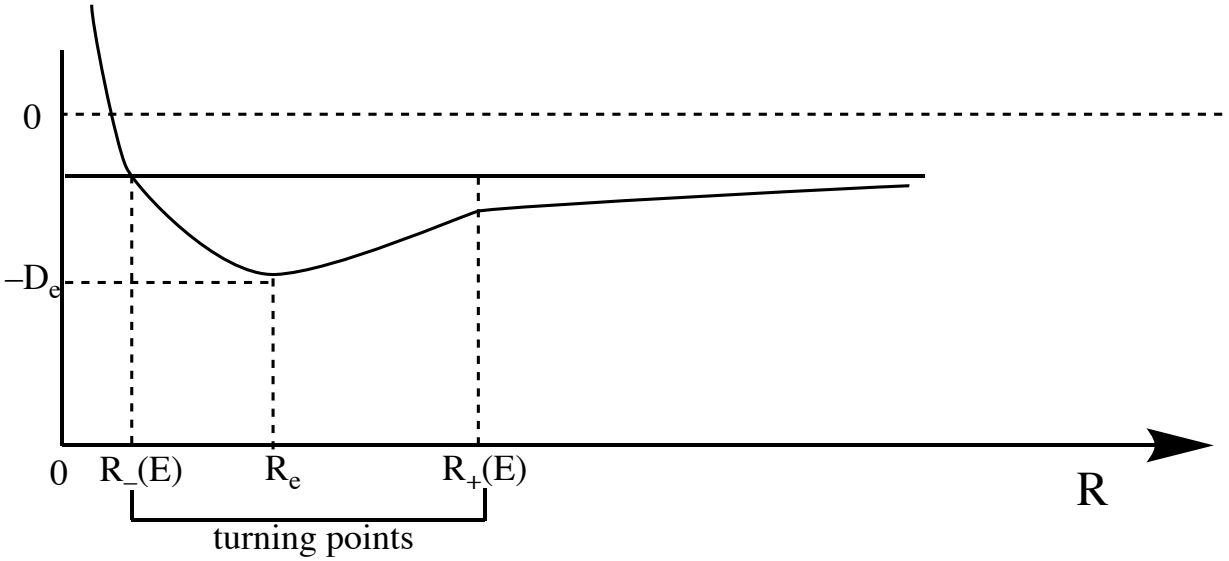
* use ψ_i to get y_i
* use ψ_i and y_i (and y_{i-1}) to get y_{i+1}
* use y_{i+1} to get ψ_{i+1}

The result is that the error in ψ_{i+1} is on the order of

$$\frac{h^6}{240}\psi_i V_i$$ — smaller error if h is smaller

(Cooley's method is much better than Euler's, which converges as a smaller power of h)

So what do we do?



$$\text{e.g., } V_{MORSE}(R) = D_e\left[1 - e^{-\beta(R-R_e)}\right]^2 - D_e \quad \text{[zero of V at dissociation]}$$

$$V(\infty) = 0, \; V(R_e) = -D_e$$

or, more generally than Morse, use $V_{J,RKR}$.

$x = R - R_e$ (displacement from equilibrium)

at $R = 0$ $\quad x = -R_e \quad \psi(-R_e) = 0$

$R = \infty \quad \psi(\infty) = 0$ } boundary conditions

The two boundary conditions are handled differently, because we want to define a finite # of equally spaced grid points (not actually necessary — see Press: he uses a variable grid spacing, which is needed to sample an infinite range of *x* with a finite number of grid points)

experience — doesn't really matter for ψ_1

* at $R = 0$ $\quad \psi_0 \equiv 0$ (required)

$\psi_1 = 10^{-20}$ (arbitrarily chosen small number, which will be corrected later upon normalization)

Use this to start the integration outward. When we discover later that we made a wrong choice for ψ_1, this is corrected merely by dividing *all* ψ_i $i \geq 1$ by an i-independent correction factor.

At large R (in the classically forbidden region), choose Ψ_n at the last grid point, x_n, to be small and use WKB *only once* to compute the *next to last grid point*. We do this because we have no reason to extend the calculation to $x \to \infty$.

$\Psi_n = 10^{-30}$ (the final grid point) (based on experience)

$$\Psi_{\text{WKB}} = |p|^{-1/2} \exp\left[-\frac{1}{\hbar} \int_{R_+(E)}^{x} |p| dx \right]$$

integrating inward from outer turning point.

$$V(x) \equiv -\frac{2m}{\hbar^2}\left(E - U(x)\right) = \frac{p^2}{\hbar^2}$$

$$|p_n| = \left[2m\left(E - U_n\right)\right]^{1/2} \equiv \hbar V_n^{1/2}$$

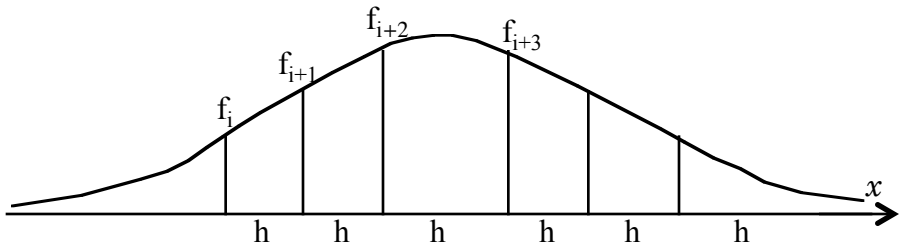
$$U_n = U\left(x_n\right)$$

WKB gives us the ratio

$$\frac{\Psi_{n-1}}{\Psi_n} = \frac{|p_{n-1}|^{-1/2} \exp\left[-\frac{1}{\hbar} \int_{R_+(E)}^{x_{n-1}} p_{n-1} dx \right]}{|p_n|^{-1/2} \exp\left[-\frac{1}{\hbar} \int_{R_+(E)}^{x_n} p_n dx \right]}$$

$p_{n-1} \approx p_n$ so pre-exponential terms cancel. Evaluate integral in exp as a sum.

$$\int_{x_-}^{x_+} f(x) dx = \sum_{i(x_-)}^{i(x_+)} \text{h} f(x_i)$$



and $e^{a+b+c} = e^a e^b e^c$, and $\dfrac{e^{a+b+c}}{e^{a+b+c+d}} = \dfrac{1}{e^d}$.

Thus, for $\dfrac{\psi_{n-1}}{\psi_n} = \dfrac{1}{\exp\left[-\dfrac{1}{\hbar}|p_n|\hbar\right]} = \exp\left[V_n^{1/2}\hbar\right]$ all of the corresponding terms in the sum cancel, leaving only the p_n term.

But we chose $\psi_n = 10^{-30}$

thus $\psi_{n-1} = 10^{-30}\exp\left[V_n^{1/2}\mathrm{h}\right]$

So we have ψ_n and ψ_{n-1} and we are off to the races.

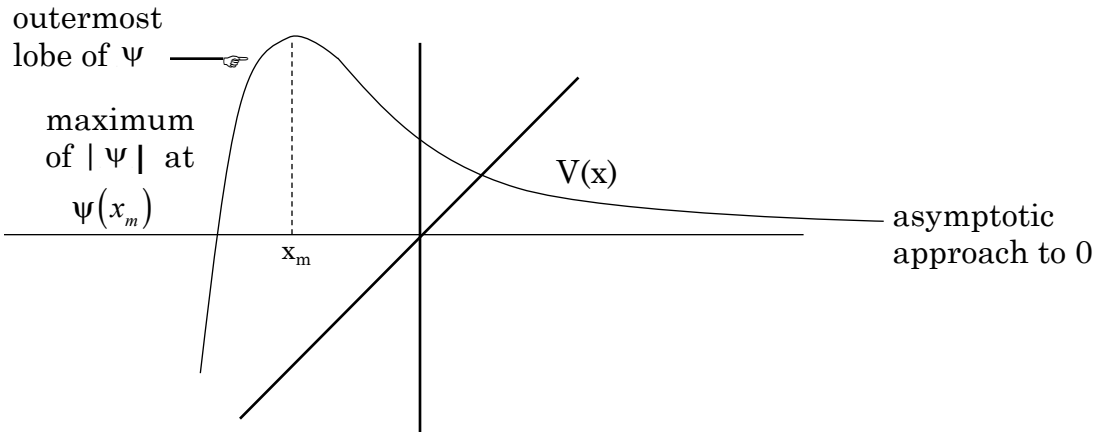
$$\psi_0 \rightarrow \psi_1 \rightarrow \psi_2 \rightarrow\rightarrow\rightarrow \psi_m \quad \vdots \quad \psi_m \leftarrow\leftarrow\leftarrow \psi_{n-1} \leftarrow \psi_n$$

m

meet in the middle at ψ_m.

Stop the inward propagation of ψ when a point is reached where, for the first time, $|\psi_m| > |\psi_{m+1}|$. This locates the *first maximum* of ψ inside the outer turning point.

Since $|\psi_i|$ is exponentially increasing from 10^{-30} at i=n until it reaches its *first maximum* inside the classically allowed region, this outer lobe of ψ is also the most important feature of ψ (because most of the probability resides in it).



Use the outermost lobe because this is the global maximum of Ψ(x). This choice minimizes the problem of precision being limited by the finite number of significant figures in the computer.

Set value of $\Psi_m = 1.0$ by renormalizing both functions

* ψ from n, n − 1, … m (from the right)	⋮	replace each ψ_i by ψ_i/ψ_m for all i down to m.
* ψ from i = 0, 1, … m (from the left)	⋮	replace each ψ_i by ψ_i/ψ_m for all i up to m.

The renormalized ψ's are denoted by Ψ'.

$$\psi'_i = \frac{\psi_i}{\psi_m} \qquad \psi'_m = 1$$

ψ′ must be continuous, especially at the joining grid point, m.

This ensures that $\psi(x)$ is continuous everywhere and that it satisfies grid form of Schr. Eq. everywhere *except* at $i = m$.

$$0 = \left(-\psi_{i+1} + 2\psi_i - \psi_{i-1}\right) + h^2 V_i \psi_i$$

In order to satisfy Schr. Eq. for $i = m$, it is necessary to adjust E. The above equation can be viewed as a nonlinear requirement on E. At the crucial grid point $i = m$, define an error function, F(E).

$$F(E) = \left(-\psi_{m+1}^E + 2\psi_m^E - \psi_{m-1}^E\right) + h^2 V_m^E \psi_m^E$$

where, by varying E, we want to search for the zeroes of F(E).

Assume that F(E) can be expanded about E_1 (E_1 is the initial, randomly chosen value of E.)

$$F(E) = F(E_1) + \left.\frac{dF}{dE}\right|_{E_1} (E - E_1) + \quad \text{discard higher terms (linearization approximation): Newton-Raphson}$$

and solve for the value of E where F(E) = 0.

Call this E_2

$$0 = F(E_1) + \left.\frac{dF}{dE}\right|_{E_1} (E_2 - E_1)$$

$$E_2 = \underbrace{-\frac{F(E_1)}{(dF/dE)_{E_1}}}_{\text{Correction to } E_1} + E_1$$

This gives an *estimate* of where the zero of F(E) nearest E_1 is located.

Usual approach: compute $\left.\frac{dF}{dE}\right|_{E_1} = \frac{F(E_1+\delta)-F(E_1)}{\delta}$

Once the derivative is known, use it to compute the trial correction to E_1 (assuming linearity).

Newton-Raphson method for solving nonlinear equation

$$E_2 = E_1 + \Delta \qquad \Delta \equiv -\frac{F(E_1)}{(dF/dE)_{E_1}}$$

Are we done? Not quite done if $F(E)$ is not sufficiently linear near E_i. Keep iterating!

Iterate until the correction, Δ, to E is smaller than a pre-set convergence criterion, ε. This seems like a lot of work, but the computer does not complain.

Now we have one not-yet-normalized eigenfunction of **H** and the corresponding eigenvalue, E.

Normalize ψ_E by dividing by $\left|\int \psi^* \psi \, dx\right|^{1/2} = N_E$

$$\int \psi^* \psi \, dx = \sum_{i=0}^{n} |\psi_i|^2 \, \mathrm{h}$$

Recall that normalization integral is evaluated by *summation* over grid points.

ψ real for bound 1-D function

box normalized: $$\psi_E(x_i) = \frac{\psi_i}{\left[\sum_j \psi_j^2 \mathrm{h}\right]^{1/2}}$$

This procedure has been used and tested by many workers. The latest and extensively documented version, "Level 16" is obtainable at Robert LeRoy's web site:

http://dx.doi.org/10.1016/j.jqsrt.2016.05.028

LEVEL: A computer program for solving the radial Schrödinger equation for bound and quasi-bound levels, Robert J. LeRoy.

I will assign some problems based on Numerov-Cooley method for integrating the 1-D Schr. Eq.

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