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

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

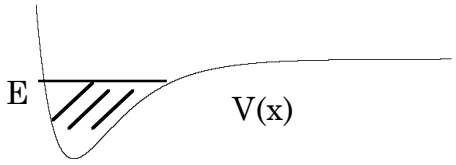
initial preparation of wp: $a_i = \int \psi_i^* [wp(x,0)] dx$

determined by $V_J(x)$

free evolution of wp

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

used WKB QC



obtained $x_{\pm}(E,J)$

Today: What do we do when we have $V_J(x)$ (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 have solved:

* piecewise constant potentials (matrix approach for joining at boundaries)
* Airy functions (linear potential and joining JWKB across turning point)
* JWKB (quantization condition and semi-classical wavefunctions)
* numerical integration (today)

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

See

1. Cooley, Math. Comput. 15, 363 (1961).
2. Press et. al., Numerical Recipes, Chapters 16 and 17

Handouts

1. Classic unpublished paper by Zare and Cashion with listing of Fortran program (now see LeRoy web site)
2. Tests of N-C vs. other methods by Tellinghuisen

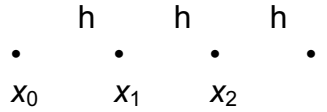
Basic Idea: grid method

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

* apply $\psi(x) = 0$ BCs at $x = 0$ and ∞ by two different tricks and then force agreement 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 $f(x_n, \psi_n)$

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

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

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:

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

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 $Å^{-2}$.

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

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

$C = 10^{-16}(8\pi^2 c\mu/h)$ h is increment of distance,

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

$(amu\ ,\ ^{12}C\ )$ cm^{-1} units (E / hc)

$$\left.\frac{d\psi}{dx}\right|_{x_i} \equiv \frac{\psi_{i+1} - \psi_i}{h}$$

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

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

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

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

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

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

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

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 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

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

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

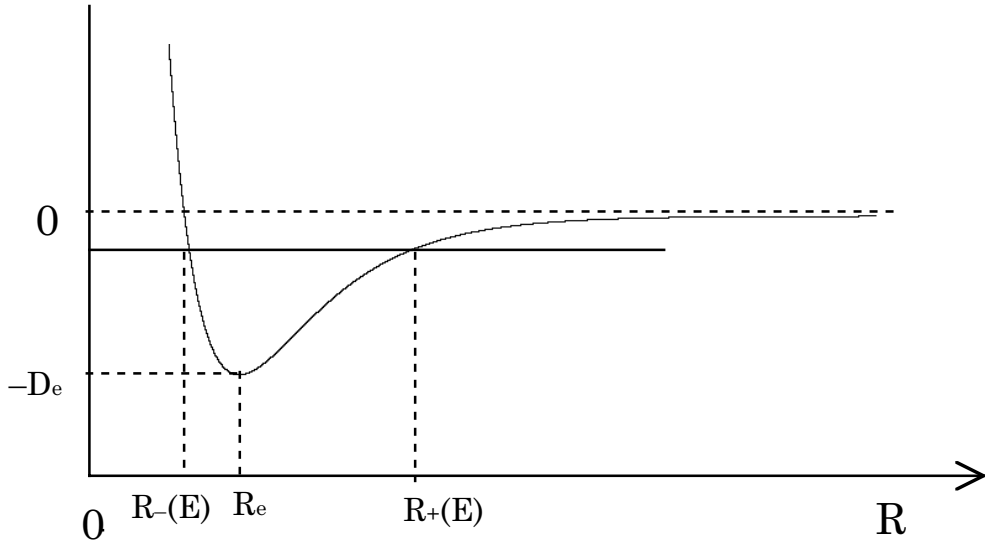
* use ψ_i to get y_i
* use ψ_i and y_i (and y_{i-1}) to get y_{i+1}
* use y_{i+1} to get ψ_{i+1}

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

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

(much better than Euler)

So what do we do?



e.g., $V_{MORSE}(R) = D_e\left[1 - e^{-\beta(R-R_e)}\right]^2 - D_e$

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

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

$R = \infty$ $\quad \psi(\infty) = 0$

} boundary conditions

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

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

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

use this to start the integration outward. If we have made a wrong choice for ψ_1, this can be corrected merely by dividing *all* ψ_i $i \geq 1$ by an i-independent correction factor.

At large R (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 go to $x \to \infty$.

$\psi_n = 10^{-30}$ (the final grid point)

$$\frac{\psi_{n-1}}{\psi_n} = \frac{e^{-R_{n-1}(V_{n-1})^{1/2}}}{e^{-R_n(V_n)^{1/2}}}$$

The next to final grid point [This is the only place WKB enters into this problem!]

$$\text{recall } \psi_{JWKB} = |p|^{-1/2} e^{-\frac{1}{\hbar}\int_{R_+(E)}^{x} |p|\,dx}$$

$$|p_n| \sim V_n^{1/2}$$

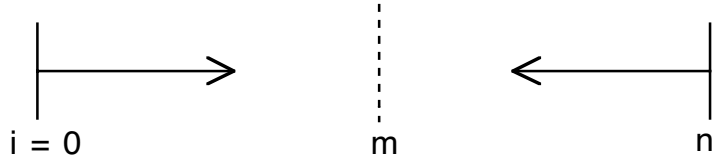
$$\text{numerator} \qquad |p_{n-1}|^{-1/2} \exp\left[-\frac{1}{h}\int_{R_+(E)}^{x_{n-1}} |p_{n-1}|dx\right]$$

$$\text{denominator} \qquad |p_n|^{-1/2} \exp\left[-\frac{1}{h}\int_{R_+(E)}^{x_n} |p_n|dx\right]$$

- pre-exponential factors are approximately equal
- integrals in exponential factors are evaluated as summations
- in ψ_{n-1}/ψ_n, the common terms in the summations in the exponential factors cancel

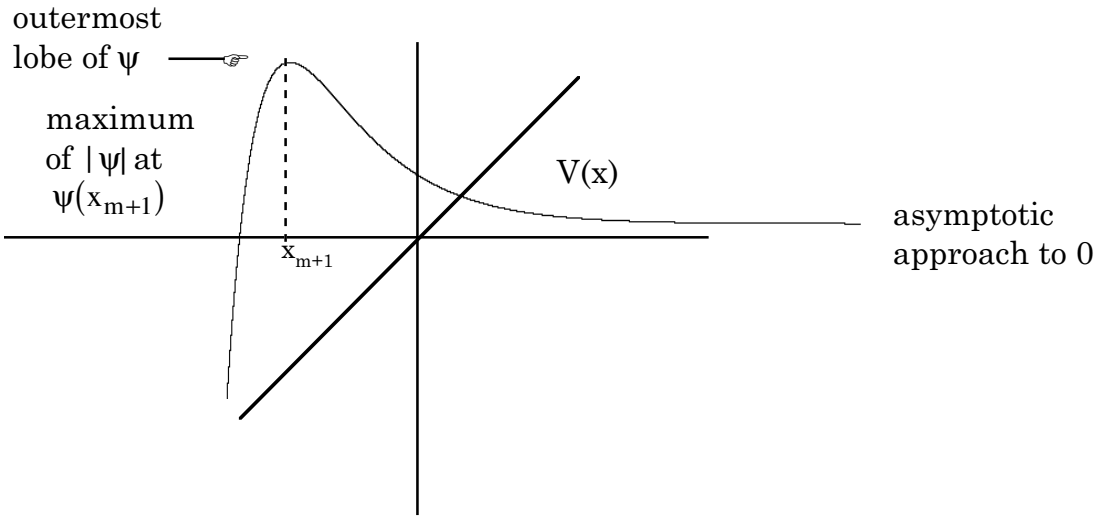
Once ψ_{n-1} is generated from ψ_n by JWKB, return to Cooley's method of numerical integration for all successive grid points.

So now we propagate one ψ from i = 0 out toward right and the other one from $i = n$ in toward the left. The "shooting" method.



Stop the inward propagation of ψ when a point is reached where, for the first time, $|\psi_m| \le |\psi_{m+1}|$.

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 outermost lobe because this is the global maximum of ψ(x), this minimizes the problem of precision being limited by 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.

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

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

The renormalized ψ's are denoted by ψ′.

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

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

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).

$$F(E) = \left(-y^E_{m+1} + 2y^E_m - y^E_{m-1}\right) + h^2 V^E_m \psi^E_m$$

where we want to search for zeroes of F(E).

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

$$F(E) = F(E_1) + \left.\frac{dF}{dE}\right|_{E_1} (E - E_1) \; + \; \text{discard higher terms}$$

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 correction to E_1 (assuming linearity).

Newton-Raphson method for solving nonlinear equation

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

Iterate until the correction, Δ, to E is smaller than a pre-set convergence criterion ε.

Now we have an eigenfunction of **H** and eigenvalue, E.

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

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

integral evaluated by summation over grid points.

ψ real for bound 1-D function

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

This procedure has been used and tested by many workers. A good version, "Level 7.1" (schrq. f), is obtainable at Robert LeRoy's web site:

http://theochem.uwaterloo.ca/~leroy/

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