Two and three dimensional problems

Grid-based methods are very time consuming
➢ number of grid points proportional to L^d

Variational methods often used in practice
➢ in atomic, molecular, solid-state physics

Variational calculations

Consider parametrized wave-function $\Psi_{\{p_i\}}(\vec{x})$

Adjust parameters p_i so that the energy is minimized

$$E[\Psi_{\{p_i\}}] = \frac{\langle \Psi_{\{p_i\}}|H|\Psi_{\{p_i\}}\rangle}{\langle \Psi_{\{p_i\}}|\Psi_{\{p_i\}}\rangle}$$

Minimization: first-order changes as $p_i \rightarrow p_i + \delta_i$ vanish

Can be very complicated for nonlinear dependence on the parameters (and the number of parameters is large)
➢ Consider linear combination of suitable basis functions

Linear variational calculations

Expansion in terms of a finite number of basis states

$$\Psi_{\{p_i\}}(\vec{x}) = \sum_{i=1}^{N} p_i \phi_i(\vec{x})$$

Leads to a **matrix eigenvalue problem** if the basis is orthogonal
➢ generalized eigenvalue problem for non-orthogonal basis
➢ the energies are above the true energies (essence of "variational")
➢ systematic improvements as size N of basis increased
➢ basis states can be adapted to the potential under study

First: Derivation of the matrix form of the Schrodinger equation

Another quantum mechanics refresher…

Relation between abstract state and its wave function

$$|\Psi\rangle = \int d\vec{x}\,\Psi(\vec{x})|\vec{x}\rangle,$$

$|\vec{x}\rangle$ describes particle localized at $\vec{x}$

delta-function overlap (scalar product) $\langle\vec{x}|\vec{y}\rangle = \delta(\vec{x}-\vec{y})$

The wave function is the overlap with the position-basis states

$$\langle\vec{x}|\Psi\rangle = \int d\vec{y}\,\Psi(\vec{y})\langle\vec{x}|\vec{y}\rangle = \int d\vec{y}\,\Psi(\vec{y})\delta(\vec{x}-\vec{y}) = \Psi(\vec{x})$$

Expansion in a complete discrete set of orthonormal states

$$|\Psi\rangle = \sum_k C_k|k\rangle, \qquad \sum_k |C_k|^2 = 1$$

position-dependent wave function in the k states

$$\phi_k(\vec{x}) = \langle\vec{x}|k\rangle$$

Expansion coefficients; wave function in k basis: $C_k = \langle k | \Psi \rangle$

If we have the real-space wave function, the coefficients are

$$\langle k | \Psi \rangle = \int d\vec{x} \int d\vec{y} \phi_k^*(\vec{x}) \Psi(\vec{y}) \langle \vec{x} | \vec{y} \rangle = \int d\vec{x} \phi_k^*(\vec{x}) \Psi(\vec{x})$$

Example of discrete basis: Momentum state in periodic box:

$$\phi_{\vec{k}}(\vec{x}) = \frac{1}{\sqrt{V}} \exp(-i\vec{k} \cdot \vec{x})$$

V = box volume. Expansion coefficients are Fourier transforms

$$C_{\vec{k}} = \frac{1}{\sqrt{V}} \int d\vec{x} e^{-i\vec{k} \cdot \vec{x}} \Psi(\vec{x})$$

Allowed wave vectors (satisfying the periodic boundary conditions)

$$\vec{k} = (k_x, k_y, k_z) = \left(n_x \frac{2\pi}{L}, n_y \frac{2\pi}{L}, n_z \frac{2\pi}{L} \right)$$

The matrix Schrodinger equation (any discrete basis)

Schrodinger equation in general operator form

$$H|\Psi\rangle = E|\Psi\rangle, \qquad (H = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}) \quad \text{in realspacebasis})$$

Use expansion in discrete basis

$$\sum_k HC_k|k\rangle = E\sum_k C_k|k\rangle$$

Rewrite Hlk> as

$$H|k\rangle = \sum_p |p\rangle\langle p|H|k\rangle = \sum_p H_{pk}|p\rangle, \qquad H_{pk} = \langle p|H|k\rangle$$

This gives

$$\sum_p \sum_k C_k H_{pk}|p\rangle = E\sum_k C_k|k\rangle$$

Requires for each p (because of orthogonality)

$$\sum_k C_k H_{pk} = EC_p$$

$$\sum_k C_k H_{pk} = E C_p$$

Corresponds to matrix equation

$$\begin{pmatrix} H_{11} & H_{12} & \cdots \\ H_{21} & H_{22} & \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \end{pmatrix} = E \begin{pmatrix} C_1 \\ C_2 \\ \vdots \end{pmatrix}$$

This is the Schrodinger equation in the k-basis
➢ Solution: diagonalization of the Hamiltonian matrix

Can be diagonalized numerically in finite basis

Variational calculation

• Chose "good" basis
• Calculate matrix elements for p,k =1 ,...,N (truncated basis)

$$H_{pk} = \langle p|H|k \rangle = \int dx^d \phi_p^*(\vec{x}) H \phi_k(\vec{x})$$

• Diagonalize the matrix

Proof that the procedure is variational (minimizes E)

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{kp} C_k C_p^* H_{kp}}{\sum_k C_k^* C_k}$$

Change δ_q in the coefficient C_q Energy becomes (leading order)

$$E(\delta_q) = \frac{\sum_{kp} C_k C_p^* H_{pk} + \sum_k (C_k \delta_q^* H_{qk} + \delta_q C_k^* H_{kq})}{\sum_k C_k C_k^* + C_q \delta_q^* + \delta_q C_q^*}$$

Can be written (leading order) as

$$E(\delta_q) = \left(E + \frac{\sum_k (C_k \delta_q^* H_{qk} + \delta_q C_k^* H_{kq})}{\sum_k C_k C_k^*} \right) \left(1 - \frac{C_q \delta_q^* + \delta_q C_q^*}{\sum_k C_k C_k^*} \right)$$

The linear shift in the energy is then

$$E(\delta_q) - E = \frac{\sum_k (C_k \delta_q^* H_{qk} + \delta_q C_k^* H_{kq})}{\sum_k C_k C_k^*} - E \frac{C_q \delta_q^* + \delta_q C_q^*}{\sum_k C_k C_k^*}$$

$$E(\delta_q) - E = \frac{\sum_k (C_k \delta_q^* H_{qk} + \delta_q C_k^* H_{kq})}{\sum_k C_k C_k^*} - E \frac{C_q \delta_q^* + \delta_q C_q^*}{\sum_k C_k C_k^*}$$

For this to vanish we must have

$$\sum_k (\delta_q^* C_k H_{qk} + \delta_q C_k^* H_{kq}) = E(C_q \delta_q^* + \delta_q C_q^*)$$

H is hermitean ->

$$\sum_k [\delta_q^* C_k H_{qk} + (\delta_q^* C_k H_{qk})^*] = E C_q \delta_q^* + (E C_k \delta_q^*)^*$$

Exactly the same condition as the matrix Schrodinger equation

- Solution of the matrix Schrodeinger equation gives extremal (minimum) values of the energies for given basis size N

- Increasing N cannot lead to higher energies, because setting $C_{N+1}=0$ gives same solution as before for C_k, k=1,...,N

- The energies must approach exact energies as N grows

So, this is a variational procedure

Matrix diagonalization

In principle, the secular equation gives eigenvalues of a matrix

$$\det[A - I\lambda] = 0$$

The eigenvectors i=1,...,N are obtained by solving

$$Av_i = \lambda_i v_i$$

Does not work well in practice (secular equation hard to solve)

Methods exist for systematically finding transformation matrix

$$D^{-1}AD = E, \quad E \text{ diagonal} \quad (D^{-1} = D^{*T})$$

Multiply by D from left; columns D_n are the eigenvectors

$$AD = DE \rightarrow AD_n = D_n E_{n,n}$$

How to proceed in practice?

➢ Read about it in Numerical Recipes or other numerics source
➢ Use Julia functions from LinearAlgebra package
   - some test examples **available (soon) on the course web site**
➢ Examples will be discussed on Friday
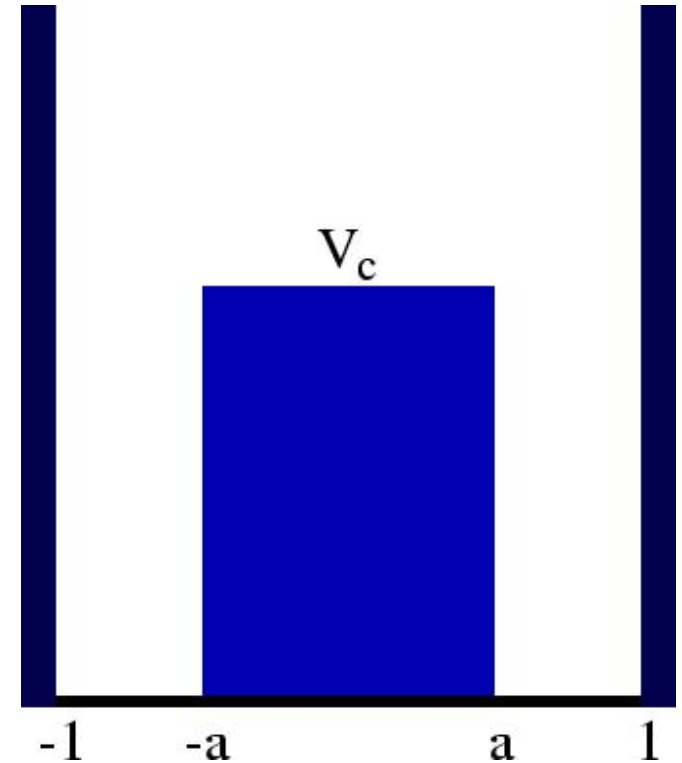
Example of variational calculation
1D square well with central barrier

Use eigenstates of pure square well (infinite walls) in variational calculation for the well with a square structure in the middle.

$$\phi_k(x) = \cos(k\pi x/2), \quad (k \text{ odd})$$
$$\phi_k(x) = \sin(k\pi x/2), \quad (k \text{ even})$$

These states are eigenstates of the kinetic energy; $K_k = k^2\pi^2/8$

$$H_{pk} = K_k\delta_{pk} + \langle p|V|k\rangle = K_k\delta_{pk} + V\int_{-a}^{a} dx\,\phi_p(x)\phi_k(x)$$

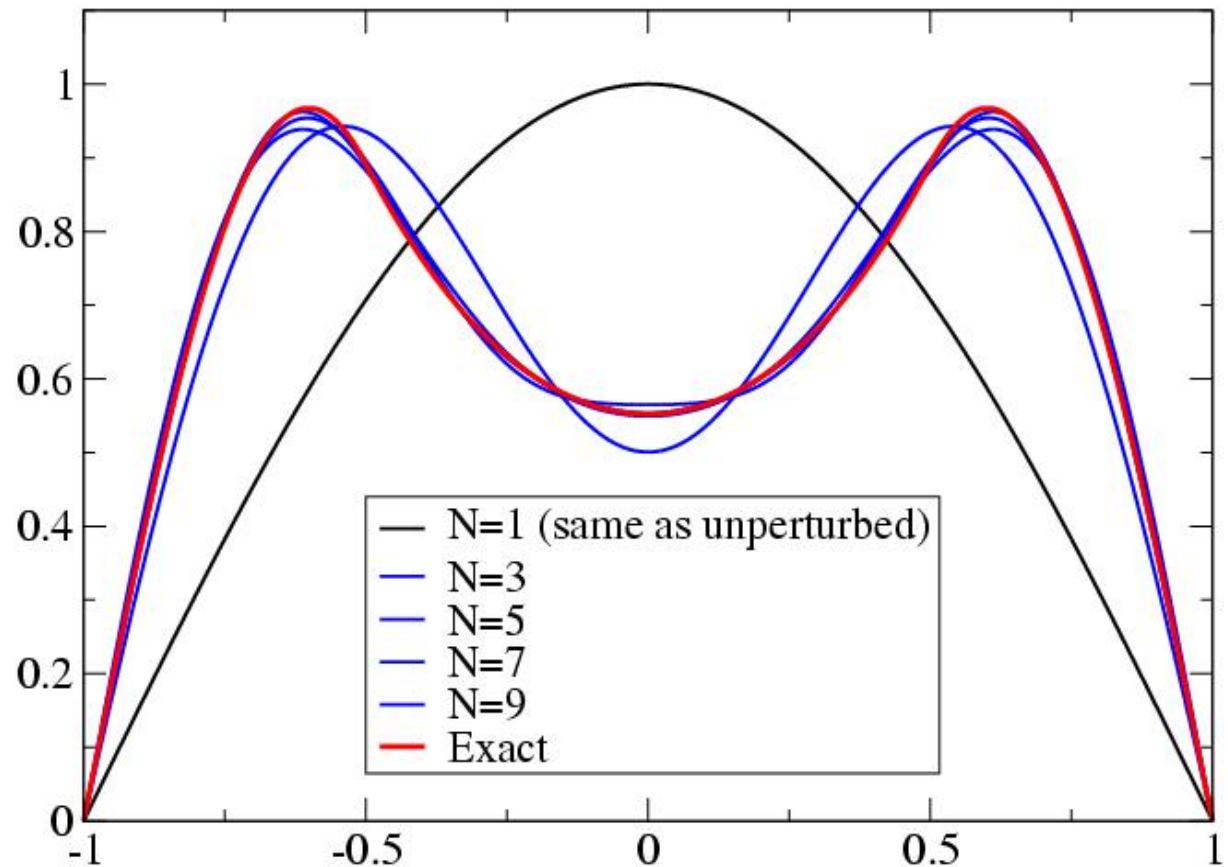How do we approach the true solution as basis size N increases?
➢ expect faster convergence for smaller V_c

$$V_c = 10 \qquad a=0.5$$

Ground state as a function of N

Wave function

N	Energy
1	9.41680
3	7.98175
5	7.79671
7	7.78016
9	7.76888
11	7.76593
13	7.76365
15	7.76276
. . .	
25	7.76105
50	7.76062

true: 7.76056

(can be obtained using the Numerov + shooting method)

How about an asymmetric barrier?

N	energy
1	8.48449
2	6.01721
3	5.06098
4	5.01719
5	4.99315
6	4.96887
8	4.96195
10	4.95900
...	
20	4.95466
...	
50	4.95407

true: 4.95402
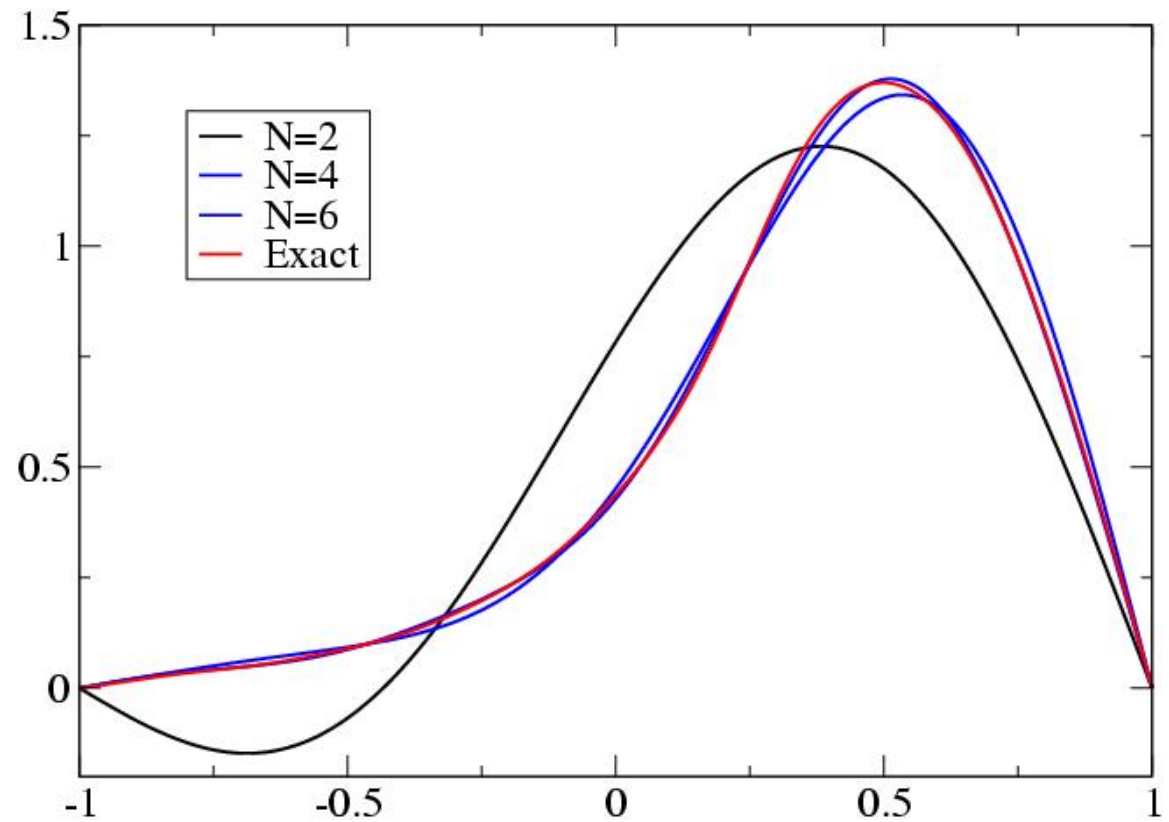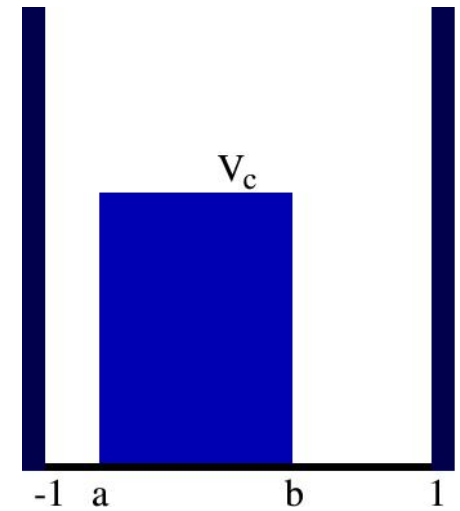
Let's do a large barrier; $V_c = 50$

What's going on?
➢ No agreement
➢ Wrong symmetry?
  (comp with Numerov)

N	energy
2	29.93480
4	14.86237
6	13.79536
8	13.62645
10	13.56317
...	
20	13.48853
30	13.47853
...	
100	13.47439

Numerov: 13.45011
(based on 10^8 steps)
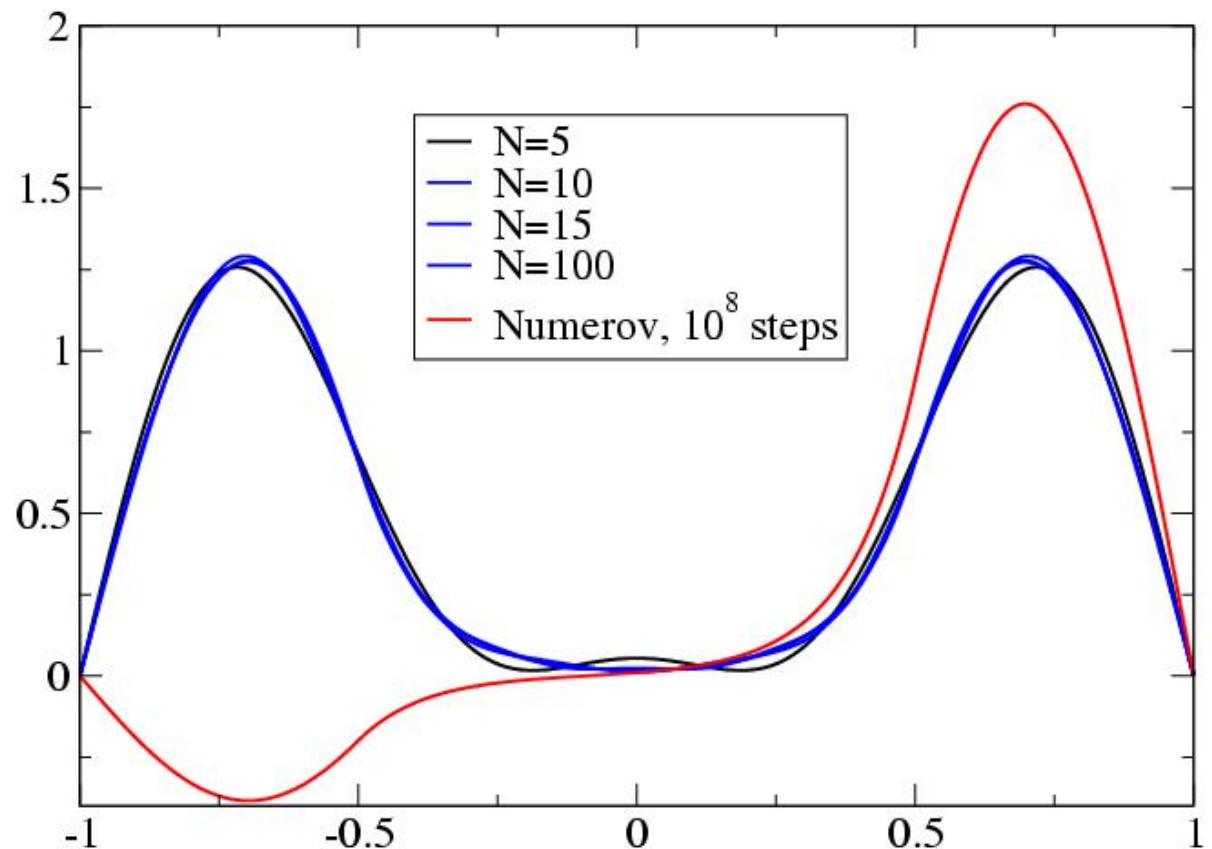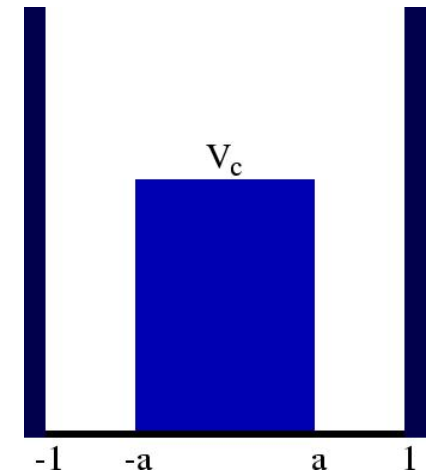
Explanation

Two almost degenerate states (symmetric/anti-symmetric)
➢ Numerical accuracy problems; Numerov mixes them
➢ The variational method easily keeps them separated
  (but larger errors in the energy)

N=20
E0=13.4885
E1=13.4904

N=100
E0=13.4744
E1=13.4773

Numerov: 13.45011
(based on 10^8 steps)