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

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

Use expansion in discrete basis

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

Rewrite H|k> as

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

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

$$A v_i = \lambda_i v_i$$

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 "canned" diagonalization routines
   - some (+ test codes) **available on the course web site**
➢ Useful subroutine library: http://gams.nist.gov
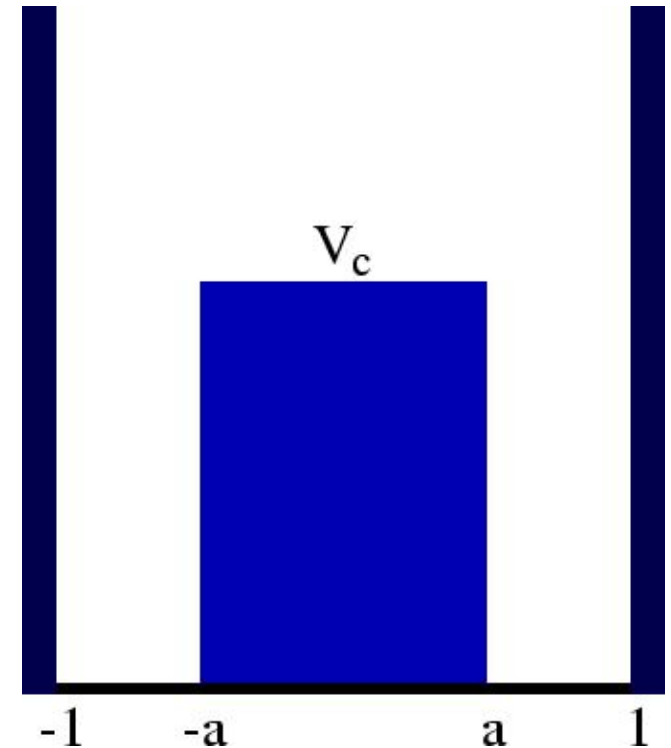
Example of variational calculation
1D square well with central barrier

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; $K_k = k^2\pi^2/8$

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

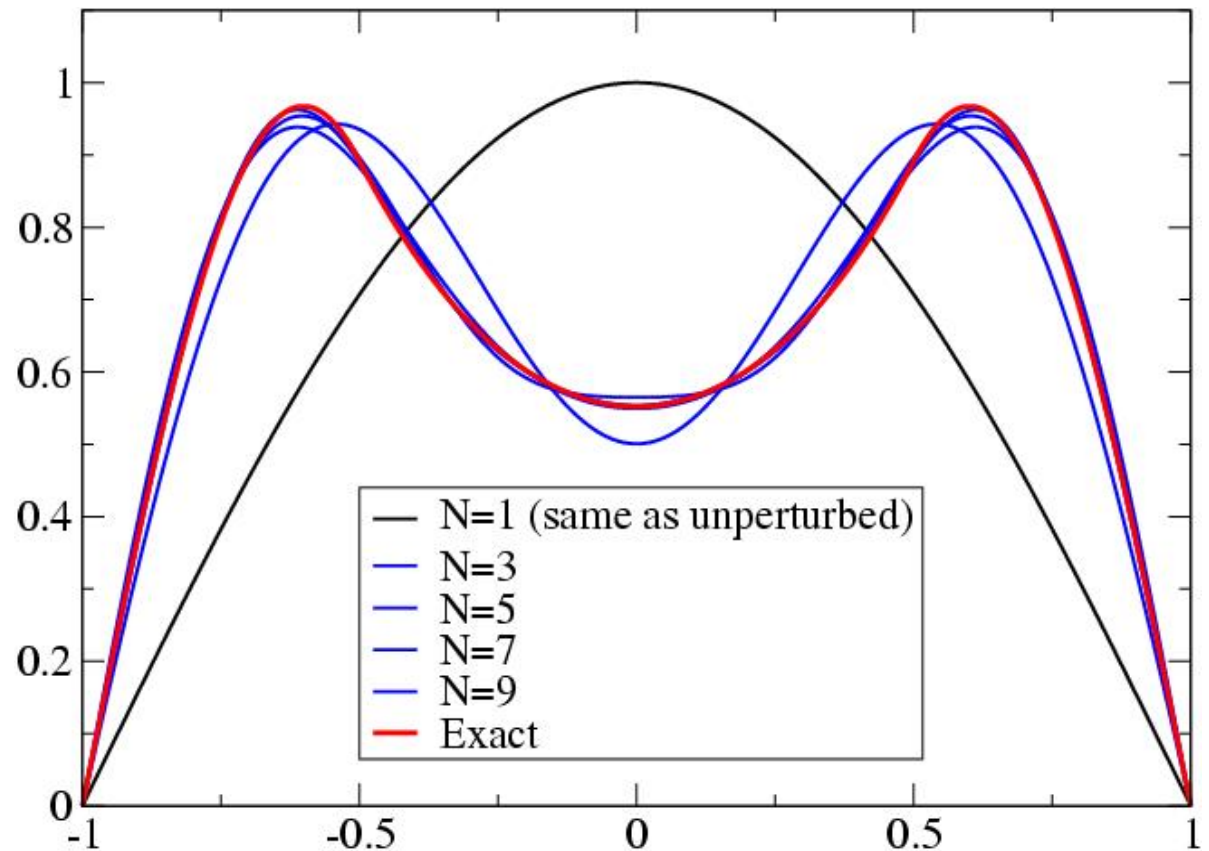How do we approach the true solution as basis size N increases?
➢ expect faster convergence for smaller V_c

$V_c = 10$ **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
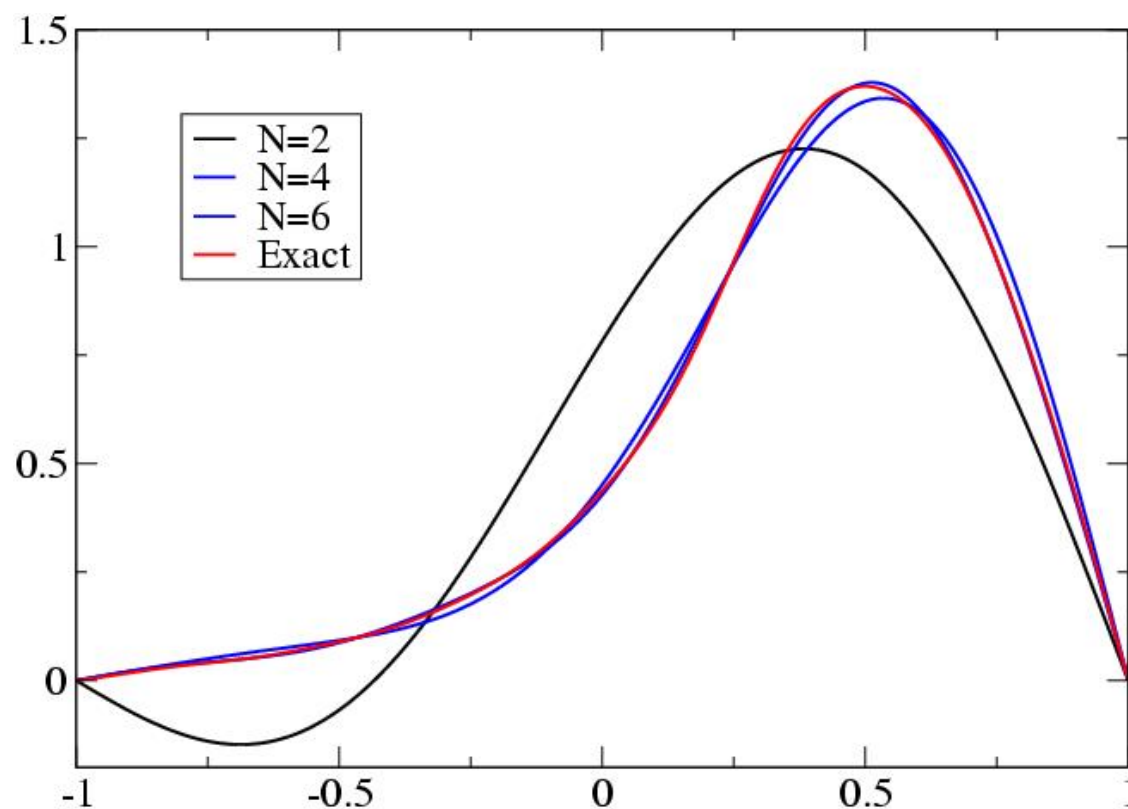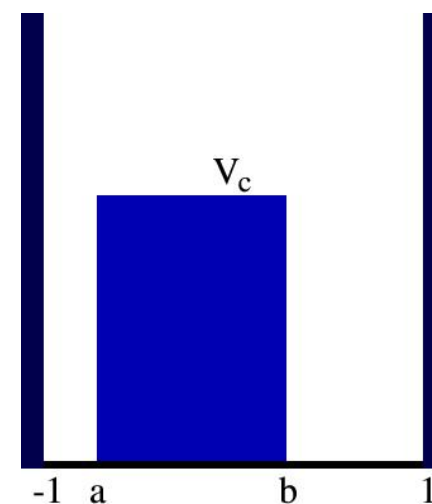
Let's do a large barrier; $V_c = 50$

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)

Legend:
— N=5
— N=10
— N=15
— N=100
— Numerov, 10^8 steps
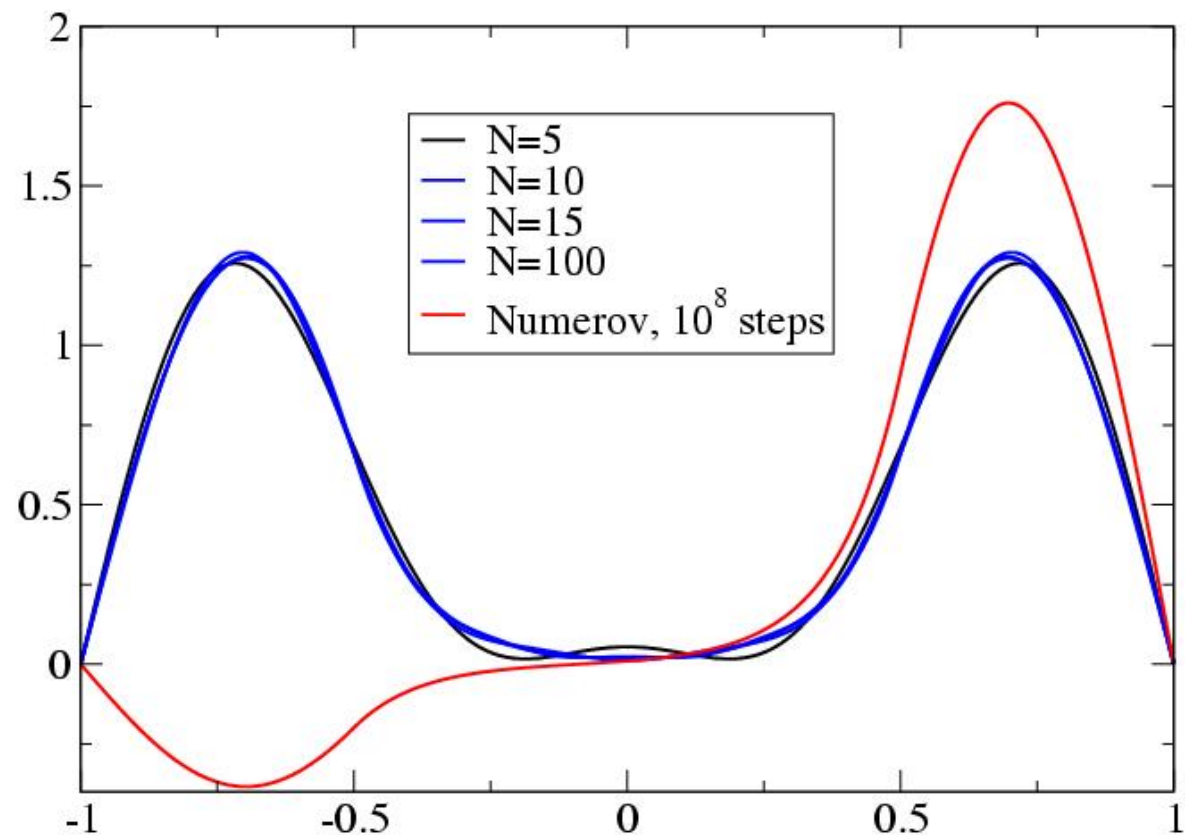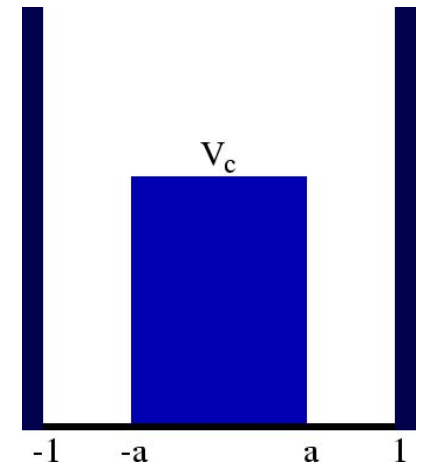
Explanation

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)