

## 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

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

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

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

Rewrite  $H|k\rangle$  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)

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

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

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  $p,k = 1, \dots, N$  (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  $\delta_q$  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 Schrodinger 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  $C_k, k=1, \dots, N$
- 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  $i=1, \dots, N$  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

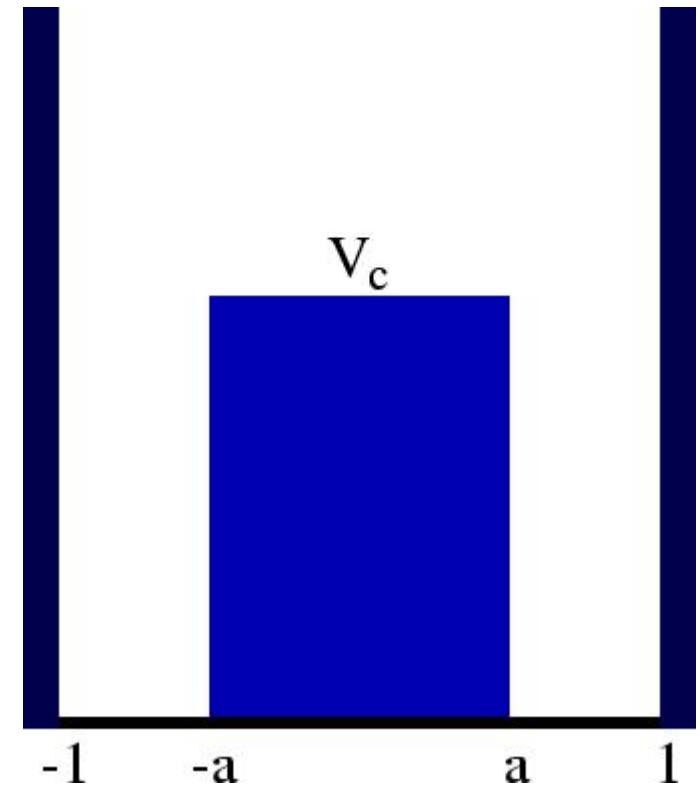
## 1D square well with central barrier

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



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

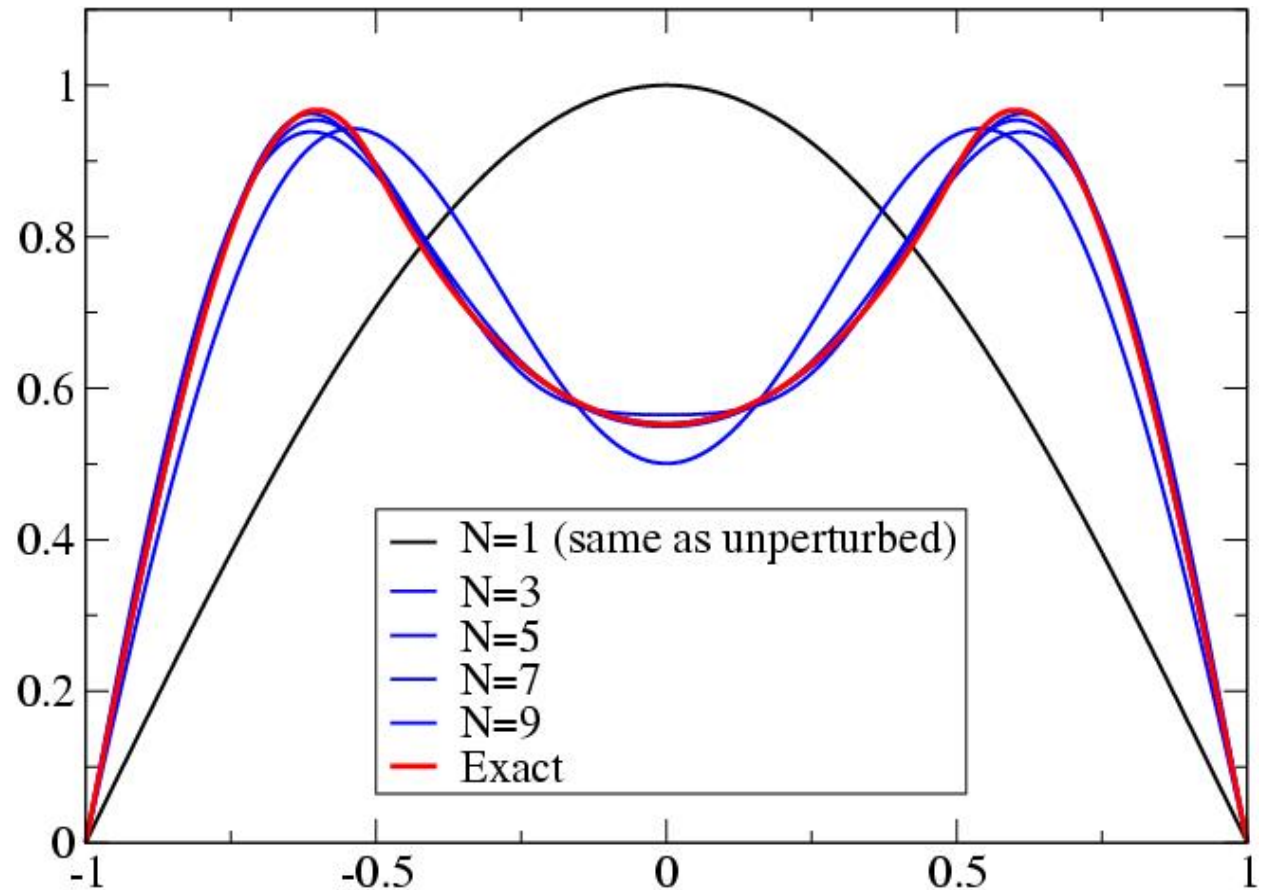
How do we approach the true solution as basis size  $N$  increases?  
➤ expect faster convergence for smaller  $V_c$

$$V_c = 10 \quad a=0.5$$

Ground state as a function of N

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

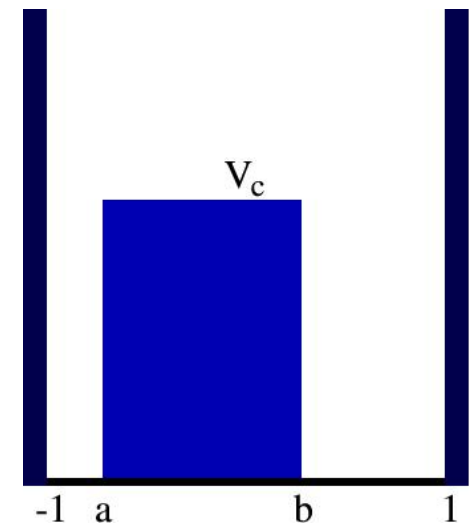
Wave function



true: 7.76056

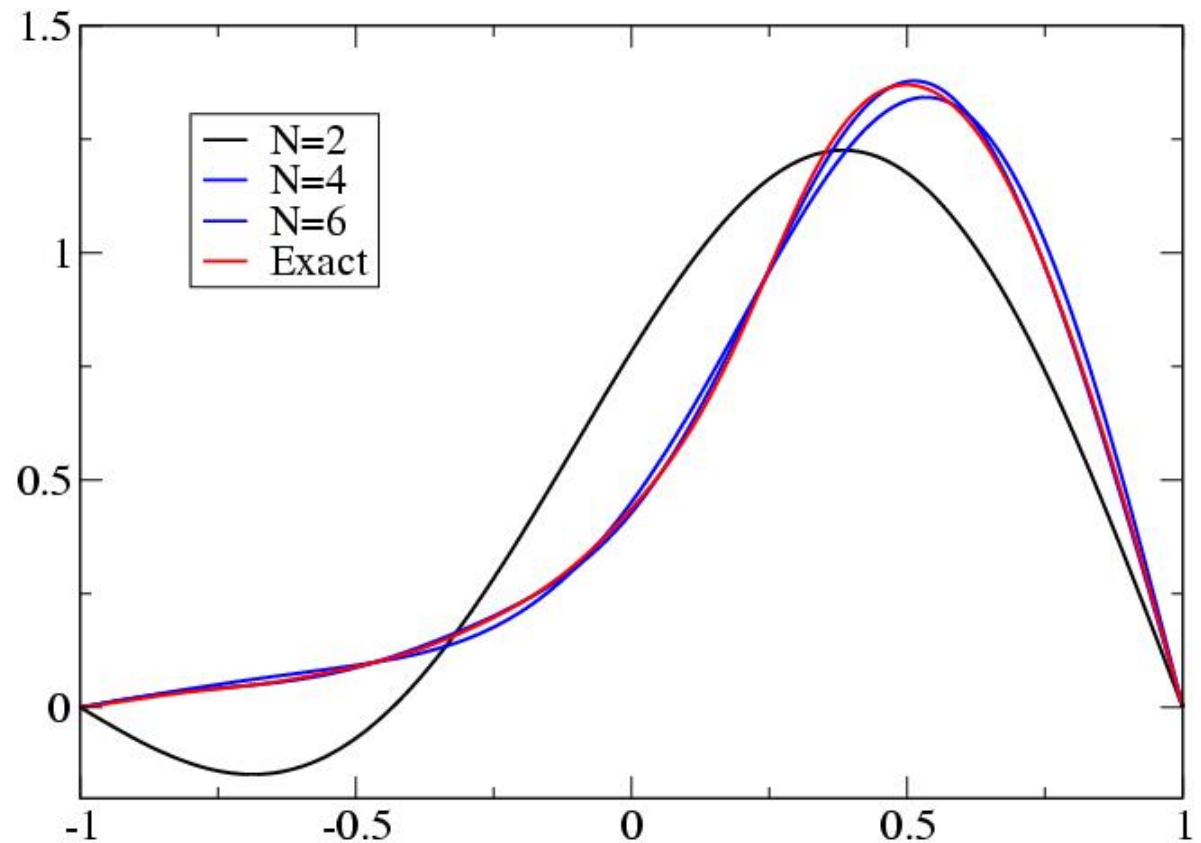
(can be obtained using the Numerov + shooting method)

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



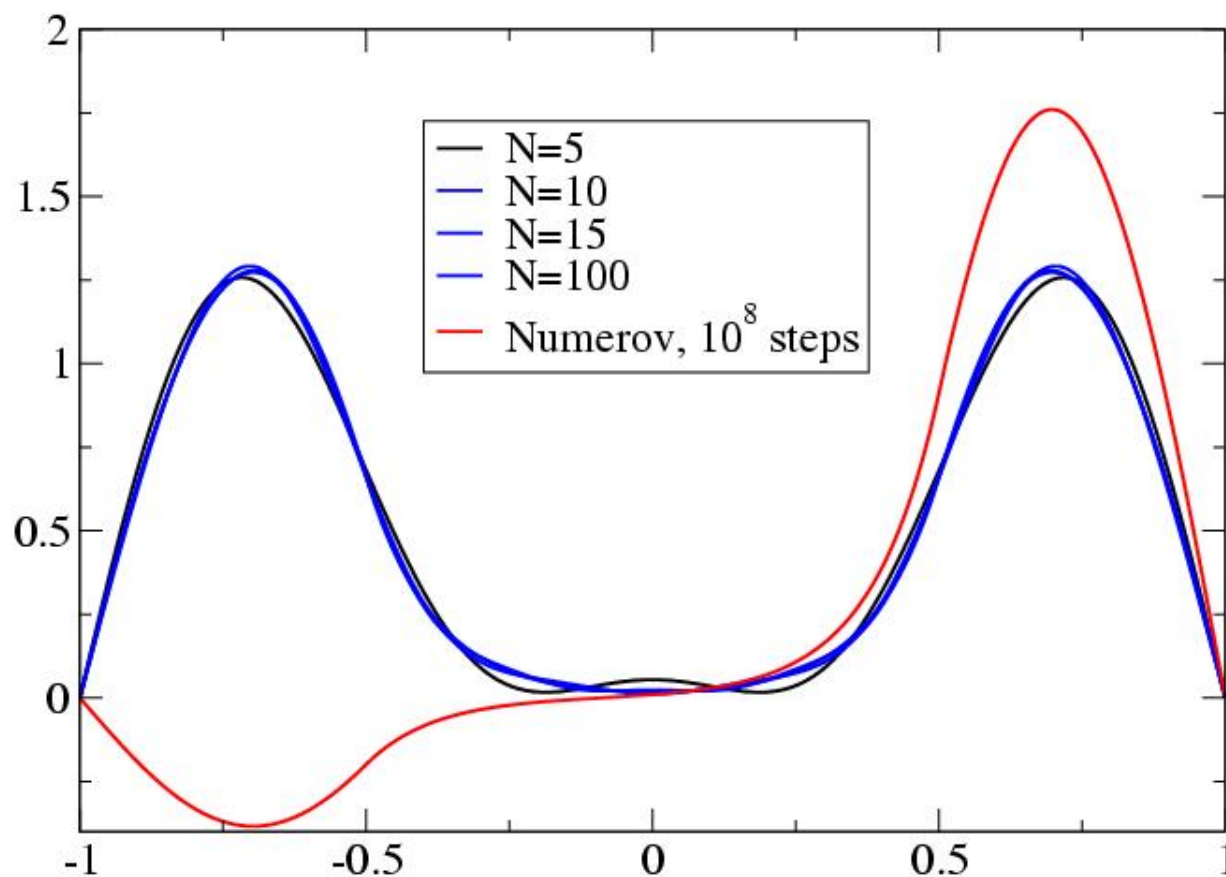
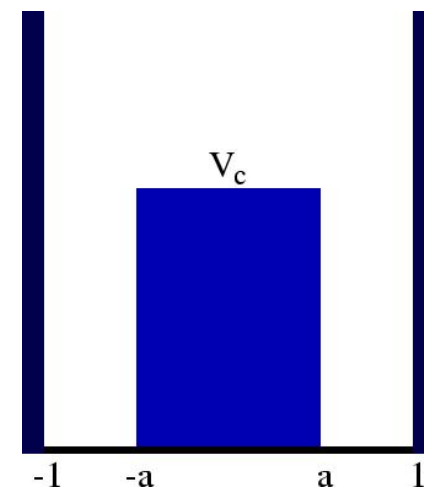
Let's do a large barrier;  $V_c = 50$

$N$	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)

What's going on?

- No agreement
- Wrong symmetry?  
(comp with Numerov)



## 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**

$E_0=13.4885$

$E_1=13.4904$

**N=100**

$E_0=13.4744$

$E_1=13.4773$

**Numerov:** 13.45011  
(based on  $10^8$  steps)

