

hydrogen atom: center-of-mass and relative

2-particle problem (electron & proton)

$$\left[-\frac{\hbar^2}{2m_e} \Delta_e - \frac{\hbar^2}{2m_p} \Delta_p + V(|\vec{r}_e - \vec{r}_p|) \right] \Psi(\vec{r}_e, \vec{r}_p) = E \Psi(\vec{r}_e, \vec{r}_p)$$

separation in center-of-mass and relative coordinates

$$\vec{R} = \frac{m_e \vec{r}_e + m_p \vec{r}_p}{m_e + m_p}$$

$$M = m_e + m_p$$

$$\vec{r} = \vec{r}_e - \vec{r}_p$$

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

$$-\frac{\hbar^2}{2M} \Delta_R S(\vec{R}) = E_{\text{CM}} S(\vec{R}) \quad \left[-\frac{\hbar^2}{2\mu} \Delta_r + V(|\vec{r}|) \right] \psi(\vec{r}) = E_H \psi(\vec{r})$$

$$\Psi(\vec{r}_e, \vec{r}_p) = S(\vec{R}) \psi(\vec{r}) \quad \text{and} \quad E = E_{\text{CM}} + E_H$$

hydrogen atom: spherical separation

relative motion

$$\left[-\frac{\hbar^2}{2\mu} \Delta_r + V(|\vec{r}|) \right] \psi(\vec{r}) = E_H \psi(\vec{r})$$

spherical symmetry

$$\psi(\vec{r}) = \frac{u(r)}{r} Y_{l,m}(\theta, \phi)$$

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) u(r) = E_H u(r)$$

dimensionless units: $\rho = \kappa r$ with $\kappa^2 = 2m|E|/\hbar^2$ and $\rho_0 = 2me^2 / (4\pi\epsilon_0 \hbar^2 \kappa)$

$$\left(\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\rho_0}{\rho} - 1 \right) u(\rho) = 0$$

hydrogen atom: radial solution

ansatz (solve asymptotics)

$$u(\rho) = \rho^{l+1} w(\rho) e^{-\rho}$$

differential equation for $L(s)$:

$$\rho \frac{d^2 w}{d\rho^2} + 2(l+1-\rho) \frac{dw}{d\rho} + (\rho_0 - 2(l+1))w = 0$$

ansatz: power series

$$w(\rho) = \sum_{k=0}^{\infty} a_k \rho^k$$

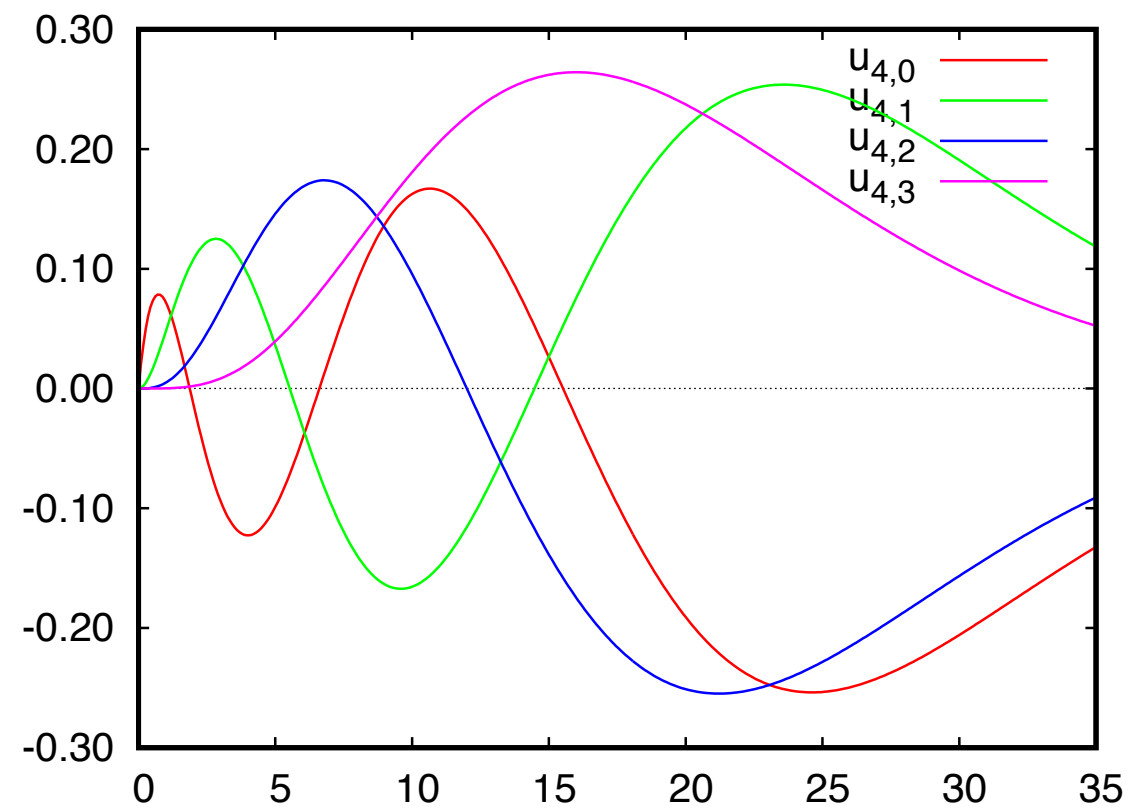
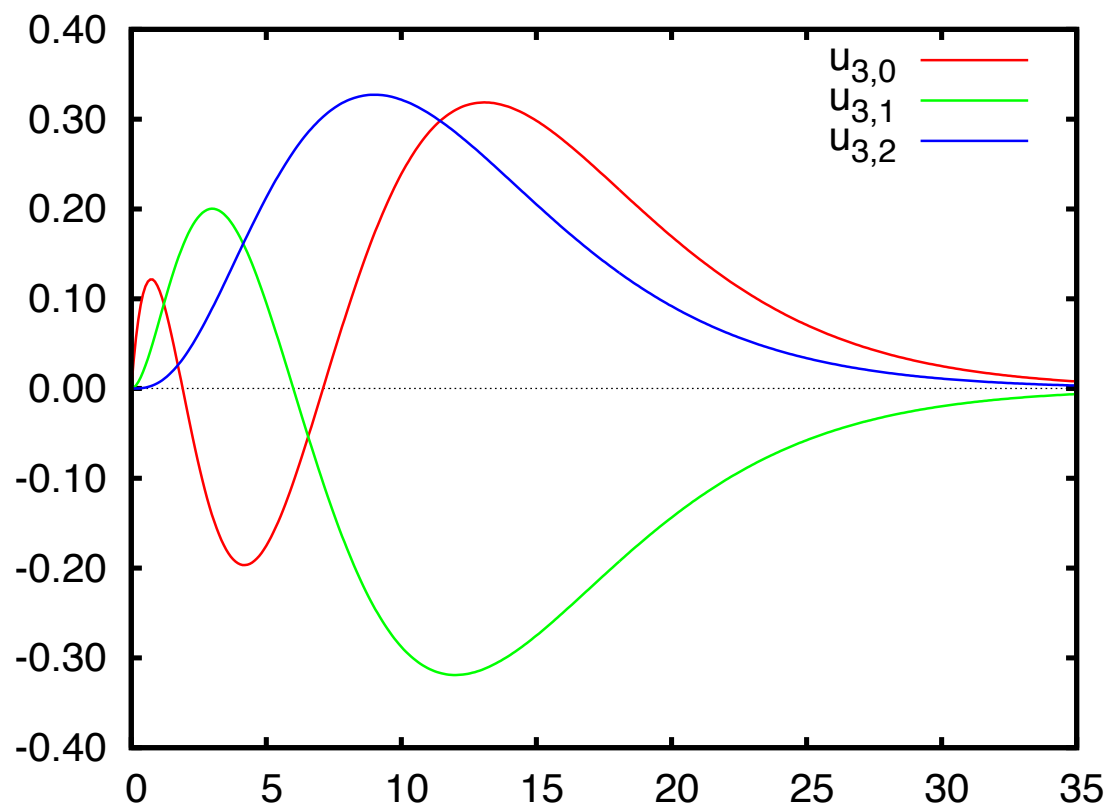
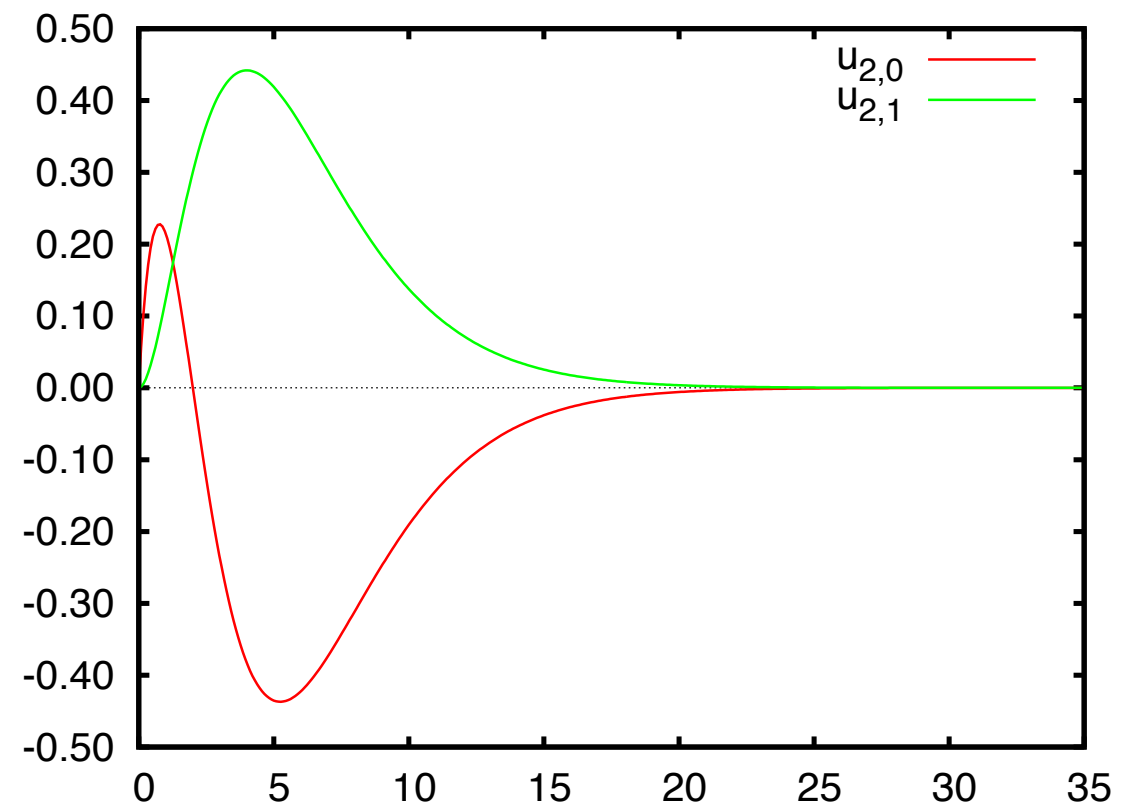
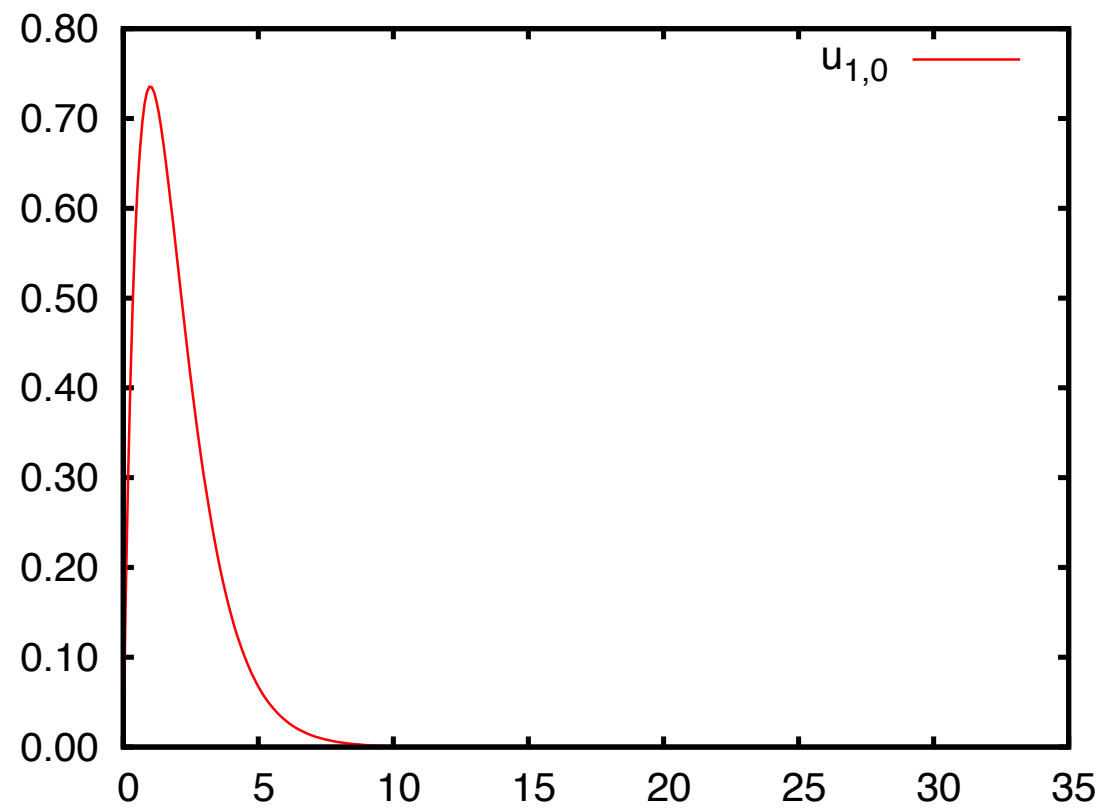
recursion for coefficients

$$a_{k+1} = \frac{2(k+l+1) - \rho_0}{(k+1)(k+2l+2)} a_k$$

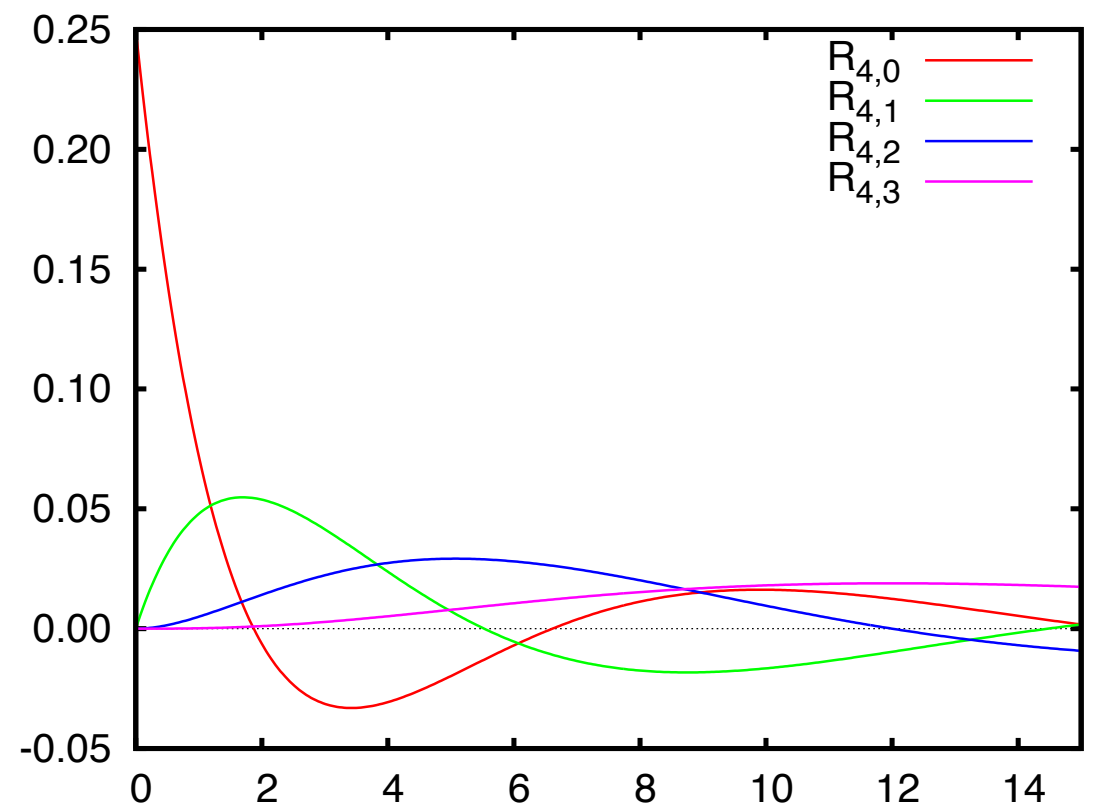
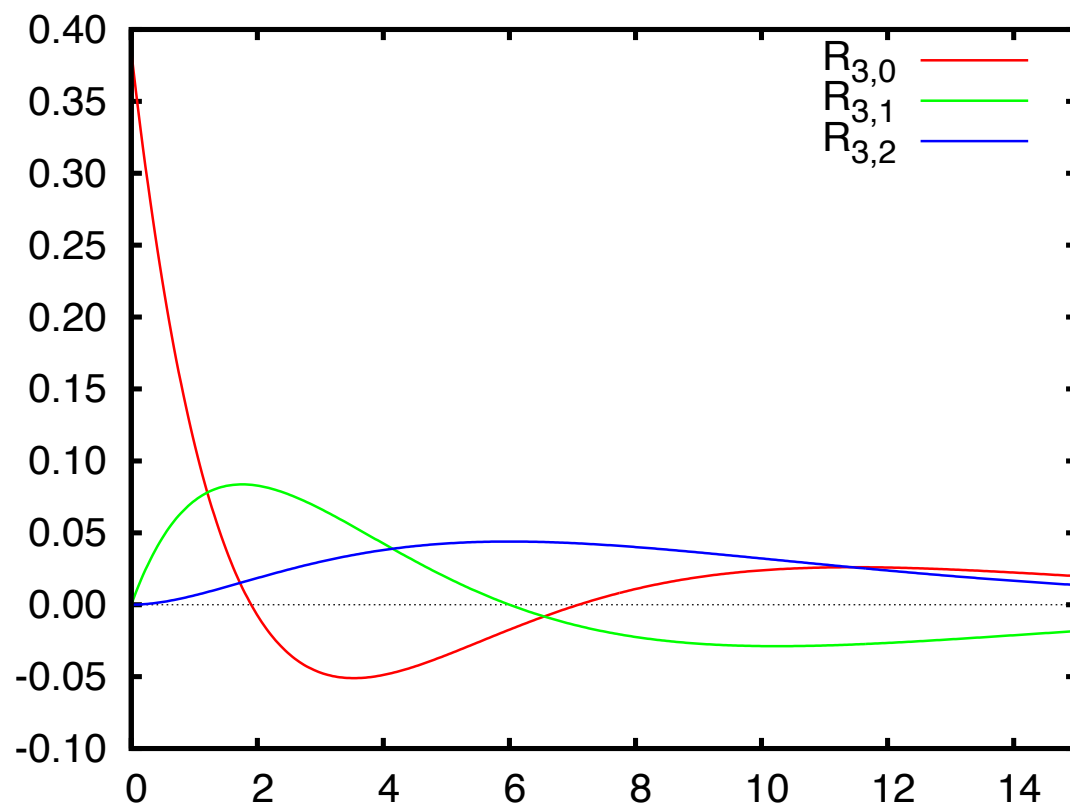
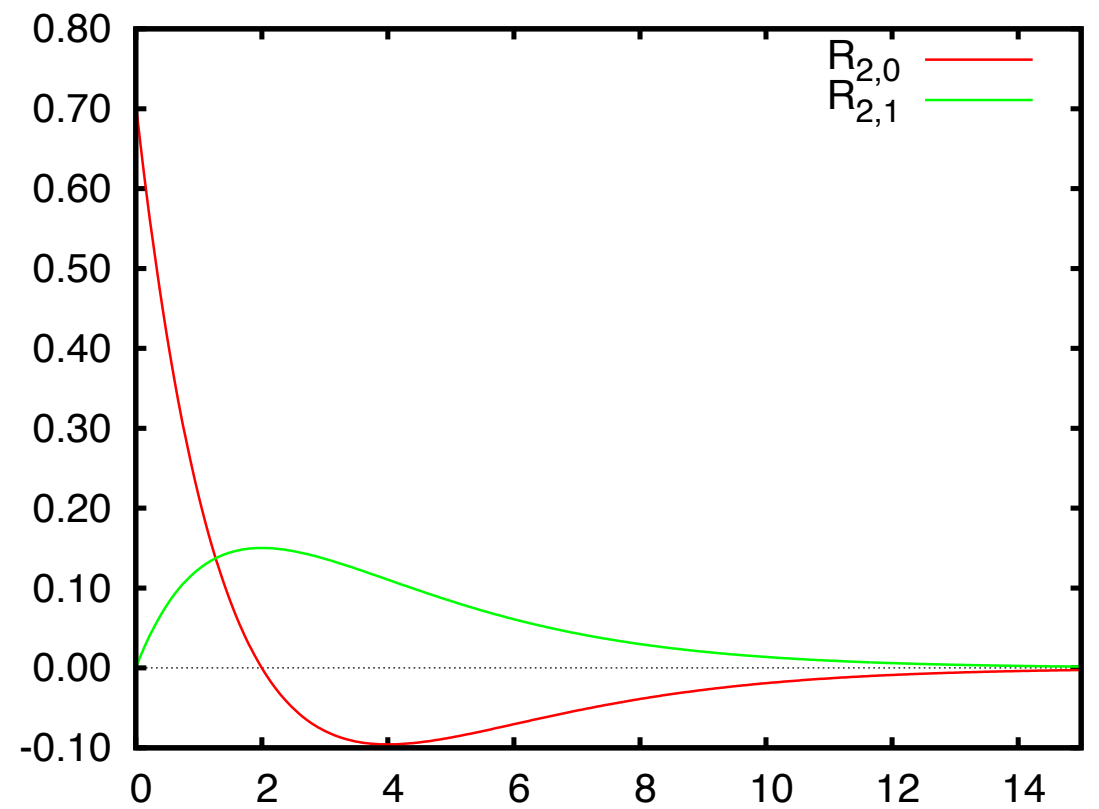
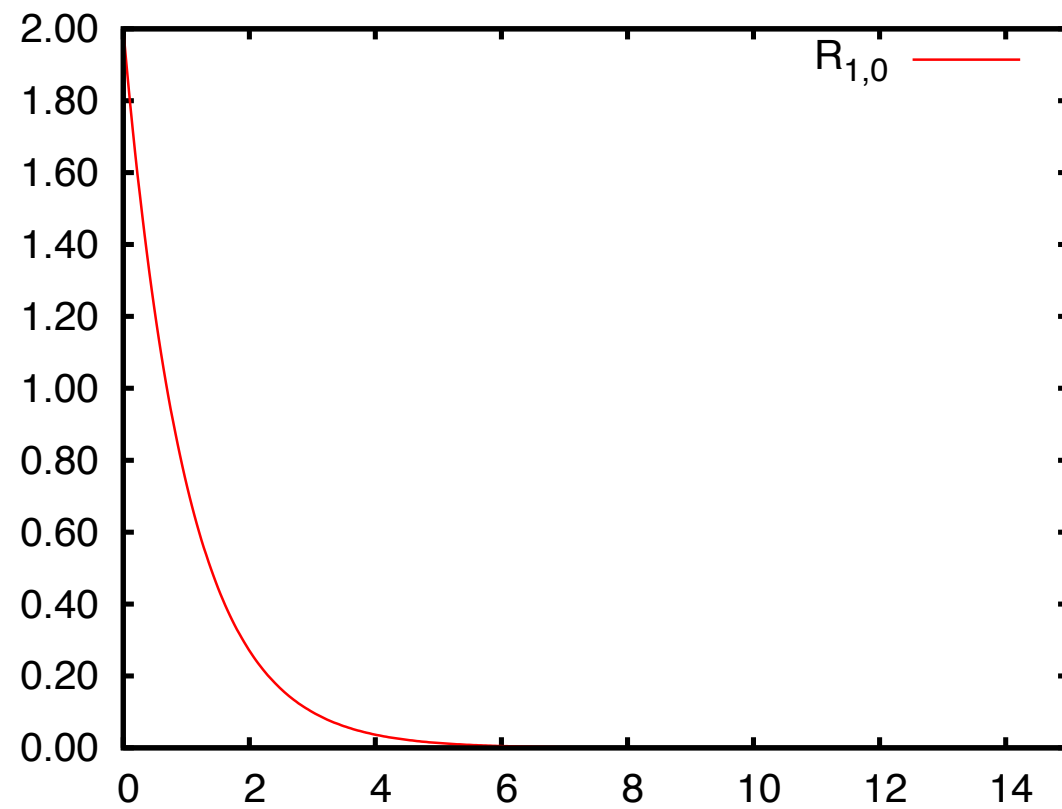
normalizability: recurrence must terminate at some finite k

$$n \geq l+1$$

radial functions $u_{nl}(r) = r R_{nl}(r)$



radial functions $R_{nl}(r)$



A simplified periodic table diagram. The elements are represented by colored blocks: yellow for alkali and alkaline earth metals (groups 1 and 2), green for transition metals (groups 3-10), red for post-transition metals (groups 11-16), and blue for nonmetals and halogens (groups 17 and 18). The layout shows the characteristic staircase shape of the periodic table.

The diagram illustrates the arrangement of atomic orbitals (AOs) in a periodic table-like structure, color-coded by type:

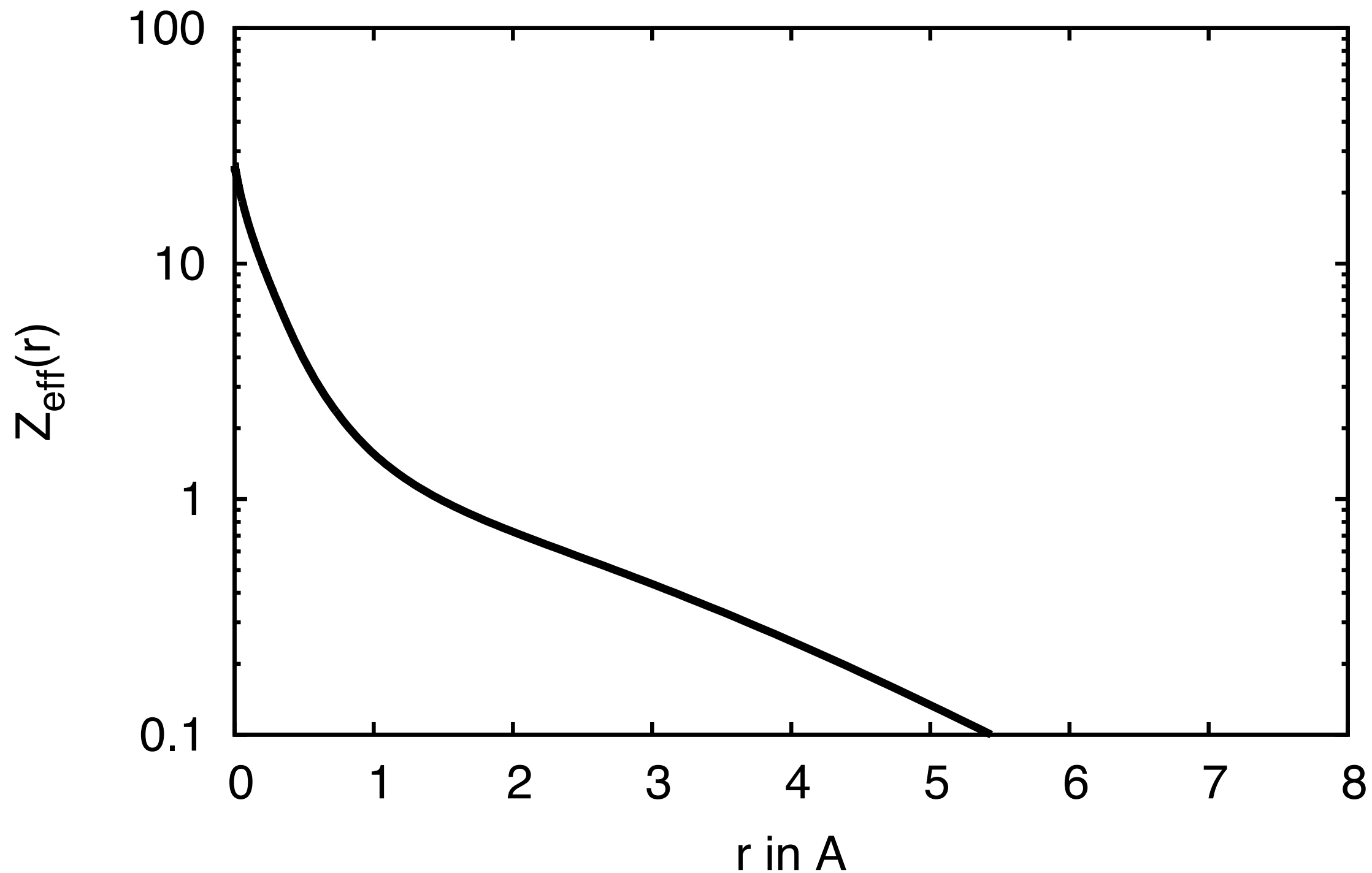
- s-orbitals (Yellow):** Located in the top-left and top-right corners. The top-left column contains 1s, 2s, 3s, 4s, 5s, 6s, and 7s. The top-right corner contains a single 1s orbital.
- p-orbitals (Blue):** Located in the top-right section. The column contains 2p, 3p, 4p, 5p, and 6p.
- d-orbitals (Red):** Located in the middle section. The column contains 3d, 4d, 5d, and 6d.
- f-orbitals (Green):** Located in the bottom section. The column contains 4f and 5f.

Electron filling is indicated by black dots in the s-orbital column:

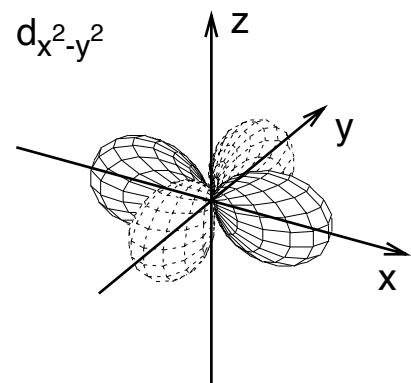
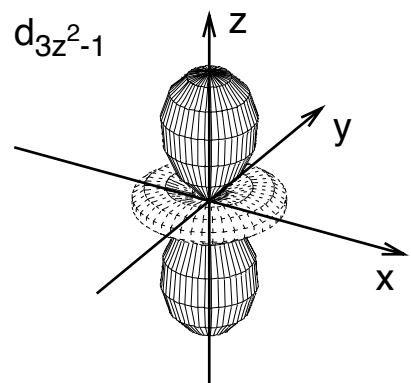
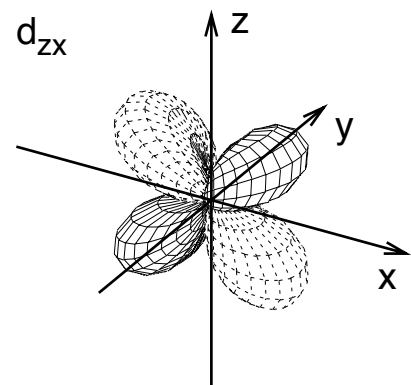
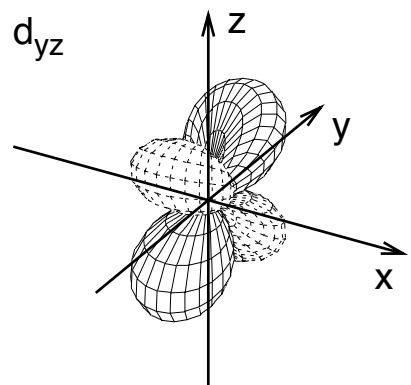
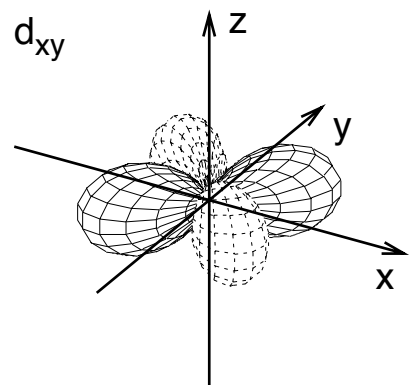
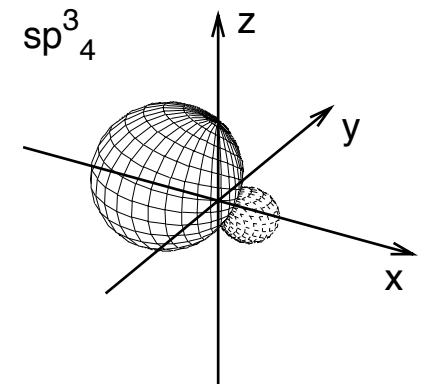
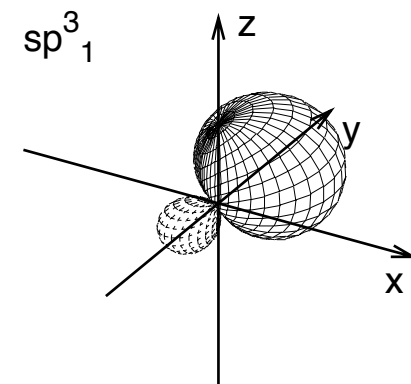
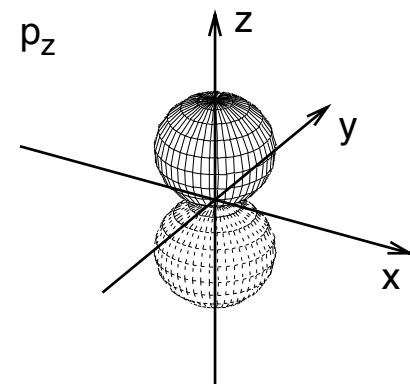
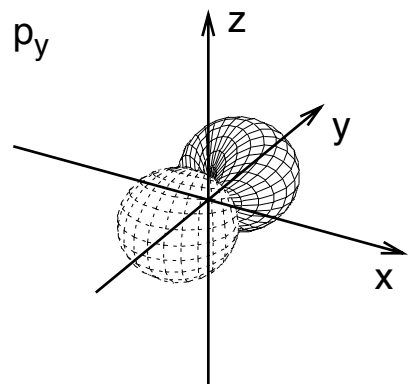
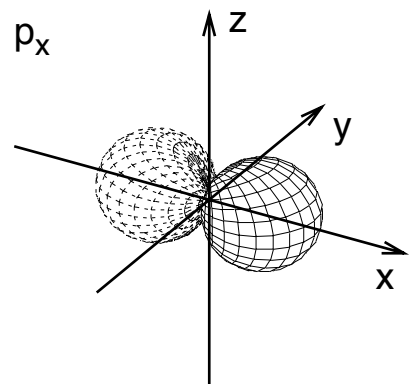
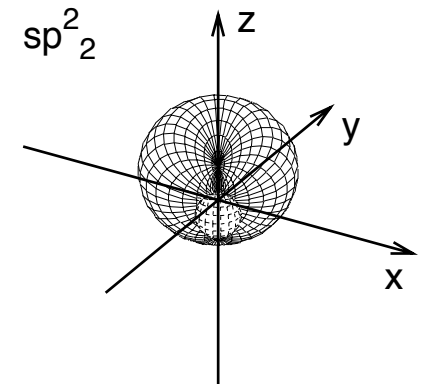
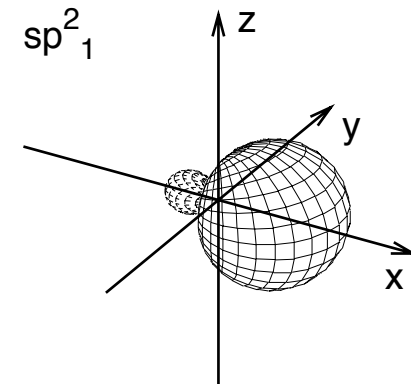
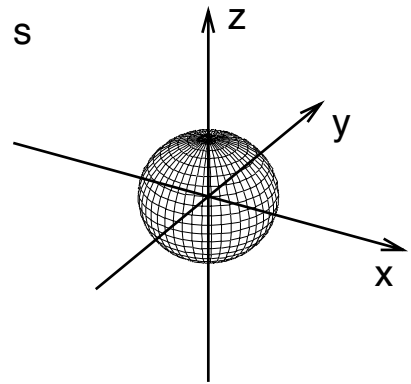
- 1s: 2 dots
- 2s: 2 dots
- 3s: 2 dots
- 4s: 2 dots
- 5s: 2 dots
- 6s: 2 dots
- 7s: 2 dots

atom in spherical mean-field approximation

Fe : [Ar] 3d⁶ 4s² 4p⁰



Atom- und Hybrid-Orbitale



numerical differentiation

task: evaluate $f'(x)$, only knowing $f(x)$ at some specified abscissae x_i

idea: approximate f by a function that can be easily differentiated, e.g., a Taylor expansion. Then combine the $f(x_i)$ such that – except for the desired derivative – as many terms as possible are cancelled.

example: first derivative

$$f(x_0 + h) = f(x_0) + h f'(x_0) + \frac{h^2}{2} f''(x_0) + \frac{h^3}{6} f'''(x_0) + \mathcal{O}(h^4)$$

$$f(x_0) = f(x_0)$$

$$f(x_0 - h) = f(x_0) - h f'(x_0) + \frac{h^2}{2} f''(x_0) - \frac{h^3}{6} f'''(x_0) + \mathcal{O}(h^4)$$

Then
$$f(x_0 + h) - f(x_0 - h) = 2h f'(x_0) + \frac{h^3}{3} f'''(x_0) + \mathcal{O}(h^4)$$

or
$$f'(x_0) = \frac{f(x_0 + h) - f(x_0 - h)}{2h} + \mathcal{O}(h^3)$$

numerical differentiation

Approximations to 1st derivative:

$$f'(x_0) = \frac{f(x_0+h)-f(x_0)}{h} + \mathcal{O}(h)$$

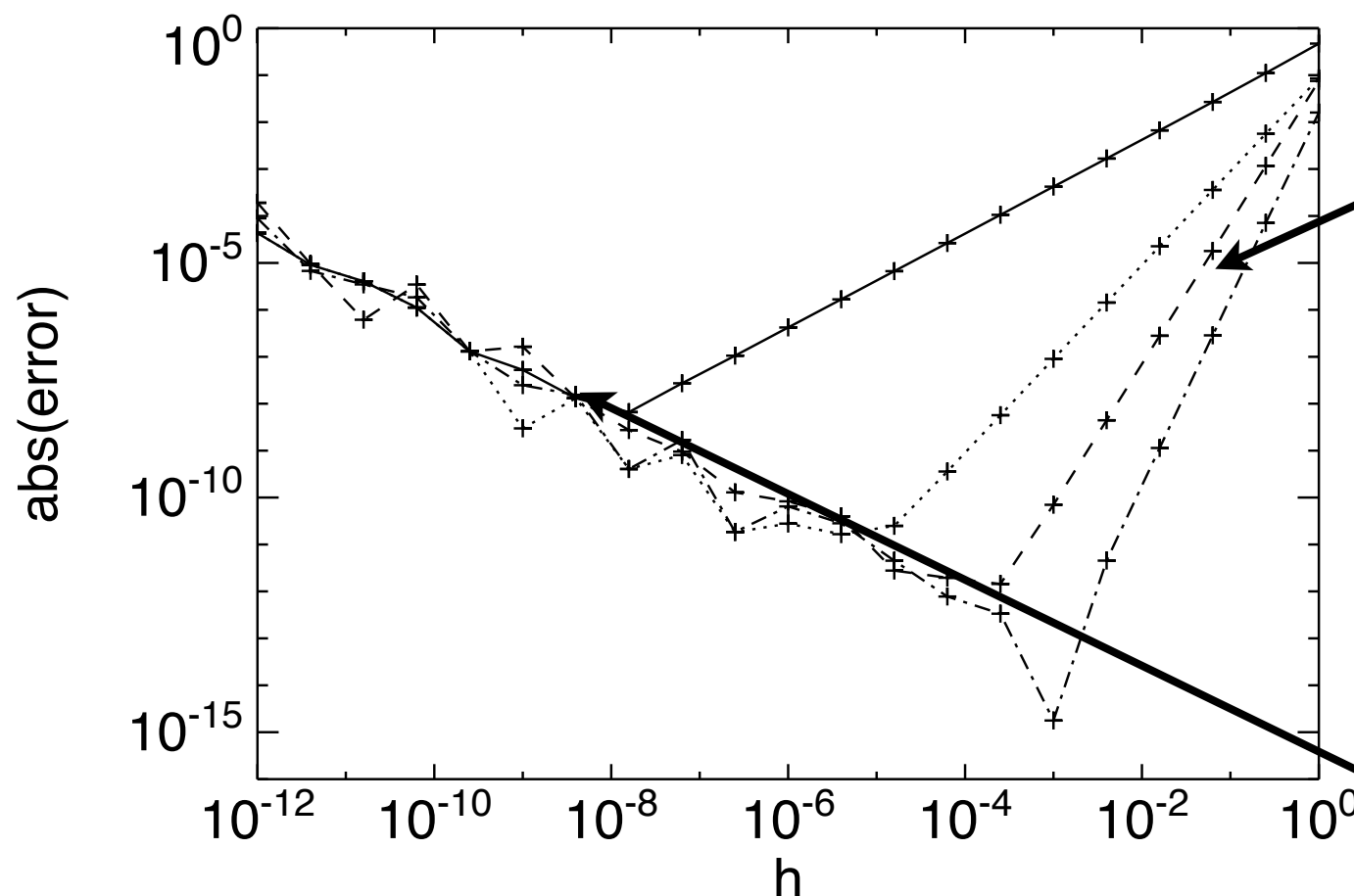
$$f'(x_0) = \frac{f(x_0+h)-f(x_0-h)}{2h} + \mathcal{O}(h^2)$$

$$f'(x_0) = \frac{-f(x_0+2h)+6f(x_0+h)-3f(x_0)-2f(x_0-h)}{6h} + \mathcal{O}(h^3)$$

$$f'(x_0) = \frac{-f(x_0+2h)+8f(x_0+h)-8f(x_0-h)+f(x_0-2h)}{12h} + \mathcal{O}(h^4)$$

differences of similar
numbers in numerator
& small denominator

example: $\sin(x)$, $x_0 = 1$



$O(h^n)$ error from
approximation

ε/h error from finite
machine accuracy ε

method of undetermined coefficients

idea: given a set of abscissae x_n , e.g., $x_n = x_0 + nh$, $n = -1, 0, 1, 2$, make an ansatz with undetermined coefficients, e.g.,:

$$f'(x_0) = \frac{\alpha_{-1}f(x_{-1}) + \alpha_0f(x_0) + \alpha_1f(x_1) + \alpha_2f(x_2)}{h}$$

determine the coefficients α_i by requiring that the formula differentiates polynomials of order, e.g., 0 to 3 exactly by solving the resulting system of linear equations

Maple session:

```
> with ( linalg ) :  
> n := 1 : # formula for nth derivative  
> mesh := [ x0-h, x0, x0+h, x0+2*h ]; p := nops(mesh) : # abscissae  $x_i$   
      mesh := [ x0-h, x0, x0+h, x0+2*h ]  
> f_x := array( [ seq( map( x -> x^k, mesh ), k=0..p-1 ) ] ); # evaluate monomials on mesh  
      f_x := 
$$\begin{bmatrix} 1 & 1 & 1 & 1 \\ x_0-h & x_0 & x_0+h & x_0+2h \\ (x_0-h)^2 & x_0^2 & (x_0+h)^2 & (x_0+2h)^2 \\ (x_0-h)^3 & x_0^3 & (x_0+h)^3 & (x_0+2h)^3 \end{bmatrix}$$
  
> der_f := array( [ seq( binomial( k, n ) * n! * x0^(k-n), k=0..p-1 ) ] );  
      # derivative of monomials  
      der_f := 
$$\begin{bmatrix} 0 & 1 & 2x_0 & 3x_0^2 \end{bmatrix}$$
  
> coefficients := linsolve( f_x, der_f ); # coefficients  $\alpha_i$   
      coefficients := 
$$\begin{bmatrix} -\frac{1}{3h} & -\frac{1}{2h} & \frac{1}{h} & -\frac{1}{6h} \end{bmatrix}$$

```

Numerov method

one-dimensional Schrödinger equation

$$u''(x) + k^2(x)u(x) = 0 \quad \text{where } k^2(x) = \frac{2m}{\hbar^2}(E - V(x))$$

numerical derivative

$$f''(x_0) = \frac{f(x_0 + h) - 2f(x_0) + f(x_0 - h)}{h^2} - \frac{h^2}{12}f^{(4)}(x_0) + \mathcal{O}(h^4)$$

two-point iteration of wave function $u(x_j)$:

$$u_{j+1} = (2 - h^2 k_j^2) u_j - u_{j-1} + \mathcal{O}(h^4)$$

Numerov trick:

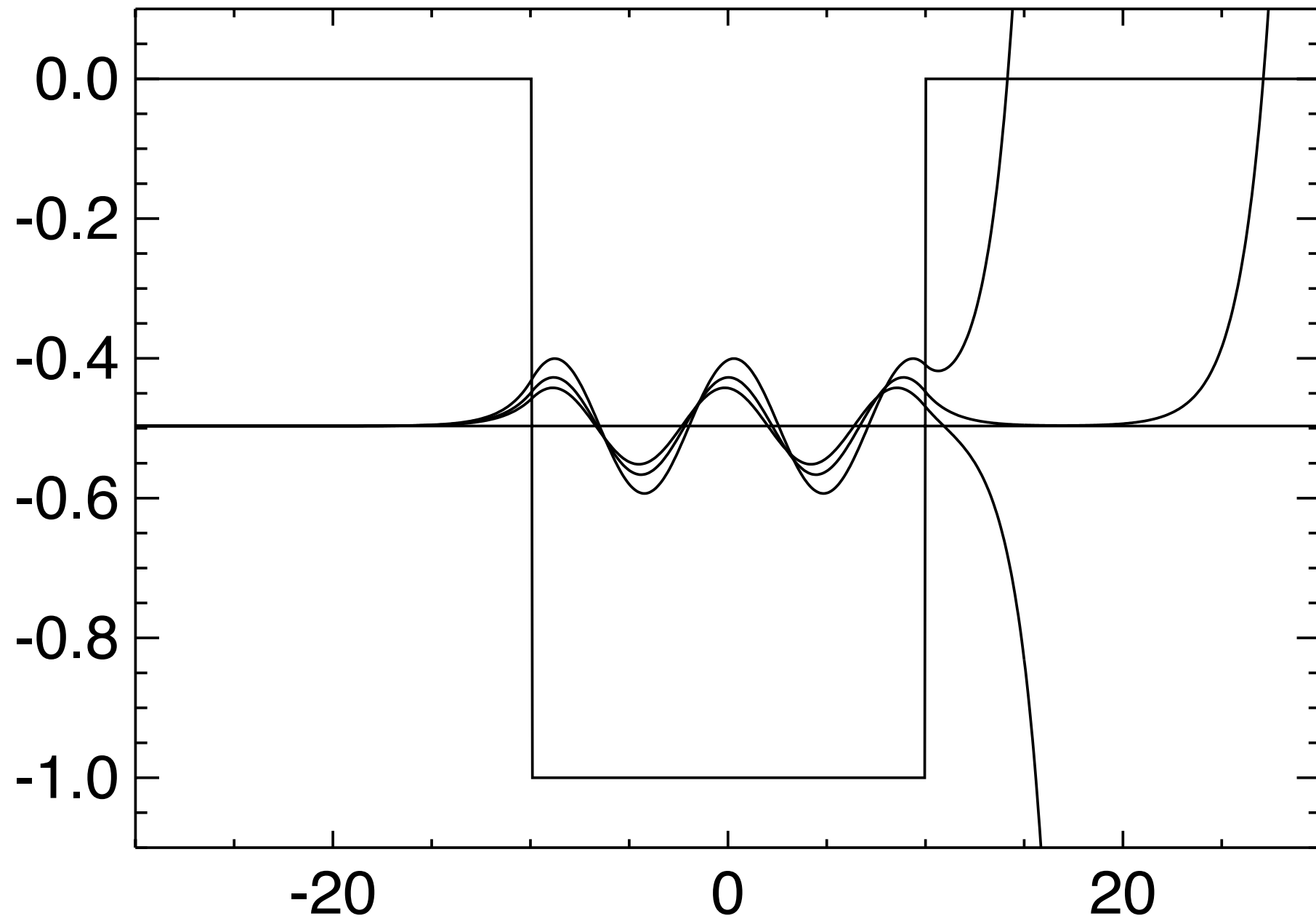
remove leading error in derivative formula by using Schrödinger equation

$$-\frac{h^2}{12}u^{(4)}(x_j) + \mathcal{O}(h^4) = +\frac{h^2}{12} \frac{d^2}{dx^2} (k^2(x_j)u(x_j)) + \mathcal{O}(h^4) = \frac{k_{j+1}^2 u_{j+1} - 2k_j^2 u_j + k_{j-1}^2 u_{j-1}}{12} + \mathcal{O}(h^4)$$

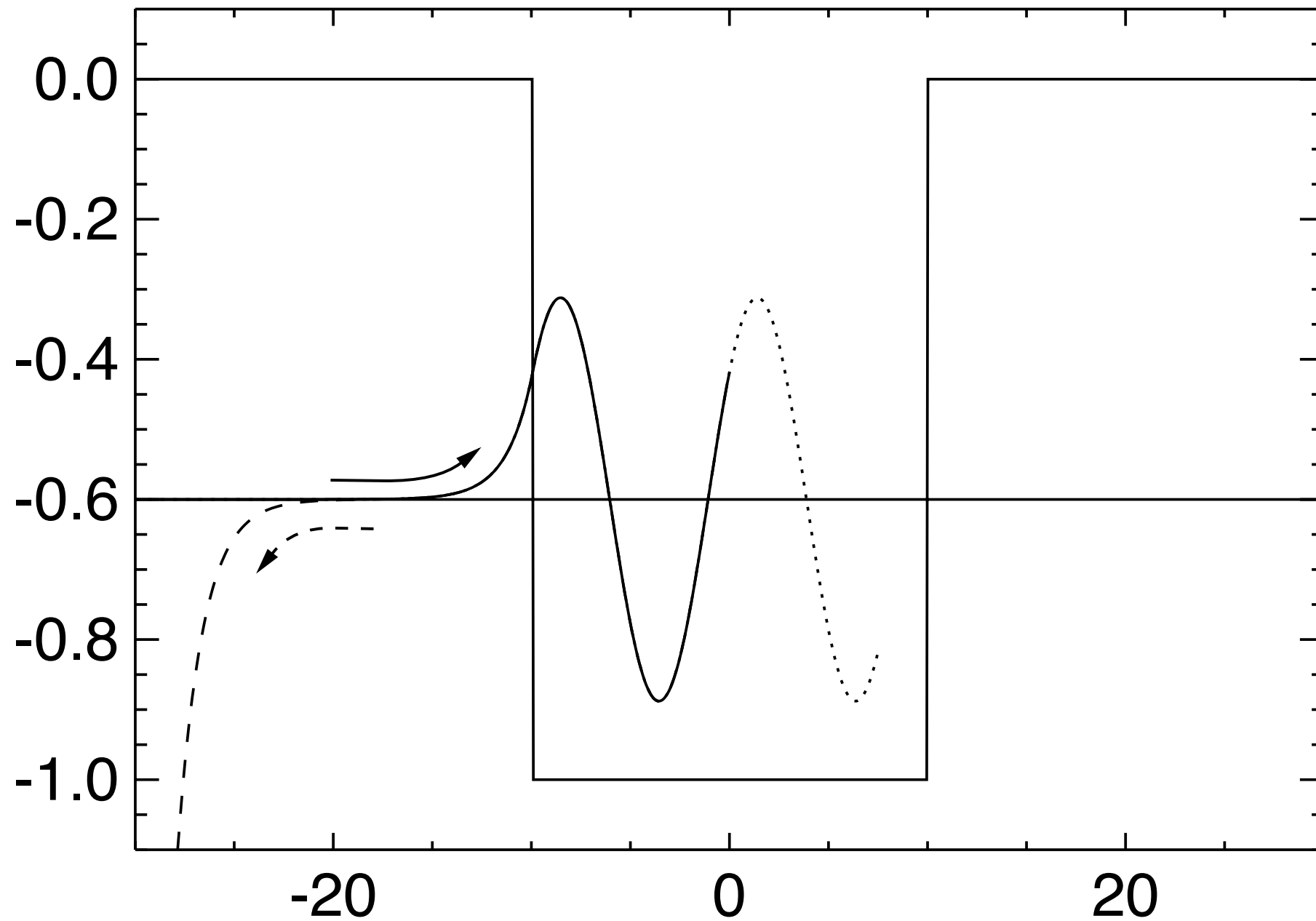
Numerov iteration:

$$u_{j\pm 1} = \frac{2(1 - 5h^2 k_j^2/12)u_j - (1 + h^2 k_{j\mp 1}^2/12)u_{j\mp 1}}{1 + h^2 k_{j\pm 1}^2/12} + \mathcal{O}(h^6)$$

Numerov iteration close to eigenvalue



(in)stability of Numerov iteration



indistinguishability and statistics

N -particle systems described by wave-function with
 N particle degrees of freedom (tensor space):

$$\Psi(x_1, \dots, x_N)$$

introduces **labeling** of particles

indistinguishable particles: no observable exists to distinguish them
in particular no observable can depend on labeling of particles

consider permutations P of particle labels

$$P\Psi(x_1, x_2) = \Psi(x_2, x_1) \text{ with } |\Psi(x_1, x_2)|^2 = |\Psi(x_2, x_1)|^2$$
$$\rightsquigarrow P\Psi(x_1, x_2) = e^{i\phi}\Psi(x_1, x_2)$$

when $P^2 = \text{Id} \Rightarrow e^{i\phi} = \pm 1$ (Ψ (anti)symmetric under permutation)

antisymmetric: $\Psi(x_1, x_2 \rightarrow x_1) = 0$ (Pauli principle)

spin-statistics connection

bosons (integer spin): symmetric wave-function

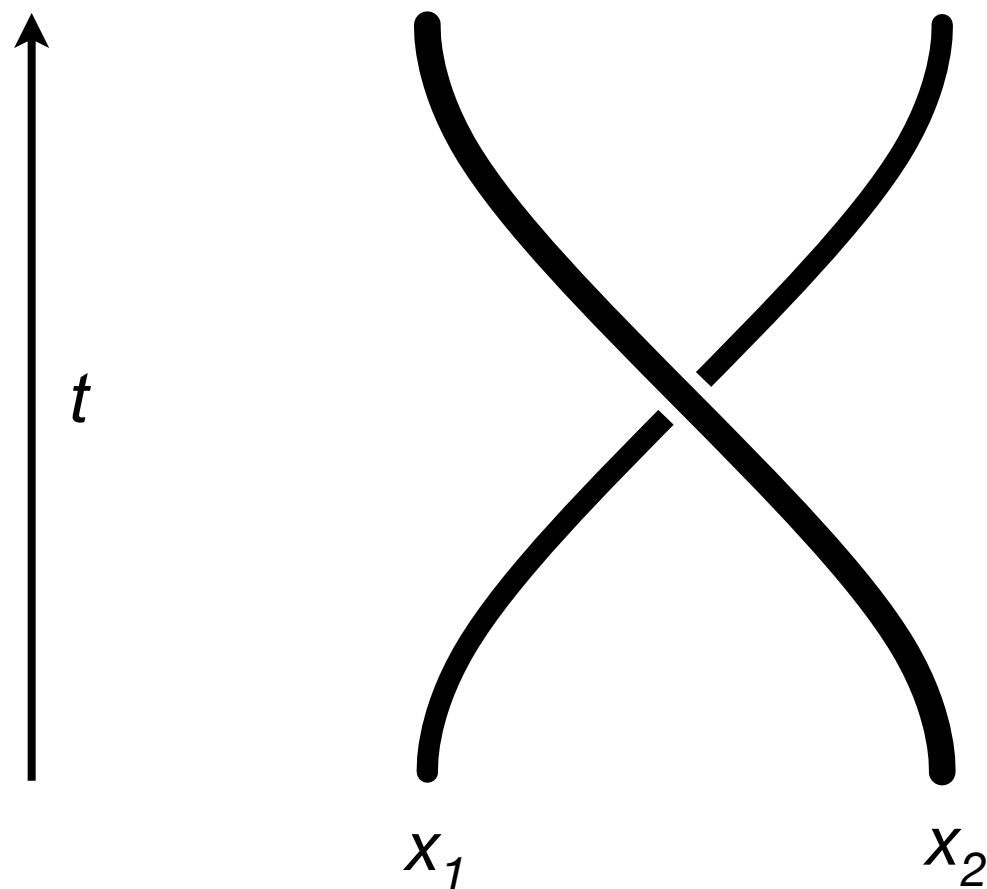
fermions (half-integer spin): anti-symmetric wave-function

Feynman Lectures III, 4-1:

Why is it that particles with half-integral spin are Fermi particles whose amplitudes add with the minus sign, whereas particles with integral spin are Bose particles whose amplitudes add with the positive sign? We apologize for the fact that we cannot give you an elementary explanation. An explanation has been worked out by Pauli from complicated arguments of quantum field theory and relativity. He has shown that the two must necessarily go together, but we have not been able to find a way of reproducing his arguments on an elementary level. It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation. The explanation is deep down in relativistic quantum mechanics. **This probably means that we do not have a complete understanding of the fundamental principle involved.** For the moment, you will just have to take it as one of the rules of the world.

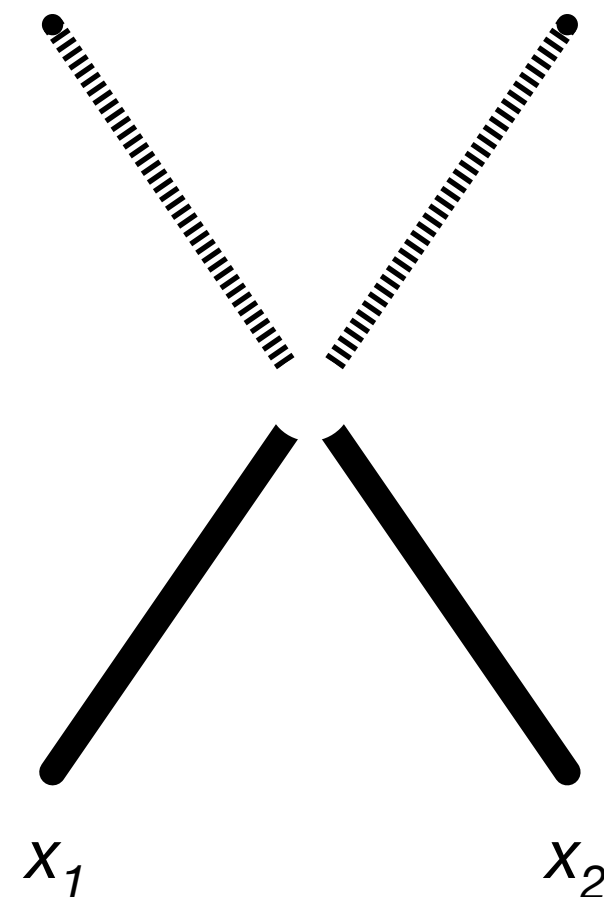
permutations in lower dimensions

M. Berry *et al.*: spin-statistics connection from geometric phase
when permuting particles along paths?



2 dimensional

$P^2 \neq \text{Id}$: *braiding* statistics: anyons



1 dimensional

fermions cannot pass

2-particle wave-function: distinguishable

two particles in (different) ortho-normal single-particle states $\varphi_a(x)$ and $\varphi_b(x)$

$$\psi_{12}(x_1, x_2) = \varphi_a(x_1)\varphi_b(x_2) \quad \text{or} \quad \psi_{21}(x_1, x_2) = \varphi_b(x_1)\varphi_a(x_2)$$

expectation value of particle distance: $M = (x_1 - x_2)^2$

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle - 2 \langle x_1 x_2 \rangle + \langle x_2^2 \rangle$$

normalized

$$\begin{aligned} \langle x_1^2 \rangle_{12} &= \int dx_1 x_1^2 |\varphi_a(x_1)|^2 \int dx_2 |\varphi_b(x_2)|^2 = \langle x^2 \rangle_a \cdot 1 \\ \langle x_2^2 \rangle_{12} &= \int dx_1 |\varphi_a(x_1)|^2 \int dx_2 x_2^2 |\varphi_b(x_2)|^2 = 1 \cdot \langle x^2 \rangle_b \\ \langle x_1 x_2 \rangle_{12} &= \int dx_1 x_1 |\varphi_a(x_1)|^2 \int dx_2 x_2 |\varphi_b(x_2)|^2 = \langle x \rangle_a \cdot \langle x \rangle_b \end{aligned}$$

$$\langle (x_1 - x_2)^2 \rangle_{12} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b$$

$$= \langle (x_2 - x_1)^2 \rangle_{12} = \langle (x_1 - x_2)^2 \rangle_{21}$$

observable does not distinguish particles

2-particle wave-function: indistinguishable

symmetric / anti-symmetric wave-function

$$\psi_{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_{12}(x_1, x_2) \pm \psi_{21}(x_1, x_2))$$

cross-terms between product wave-functions

observable does not distinguish particles

$$\langle M \rangle_{\pm} = \frac{1}{2} \left(\langle M \rangle_{12} \pm \langle \psi_{12} | M | \psi_{21} \rangle \pm \langle \psi_{21} | M | \psi_{12} \rangle + \langle M \rangle_{21} \right) = \langle M \rangle_{12} \pm \langle \psi_{12} | M | \psi_{21} \rangle$$

particle permutation: **exchange-terms**

orthogonal

$$\langle \psi_{12} | x_1^2 | \psi_{21} \rangle = \int dx_1 x_1^2 \overline{\varphi_a(x_1)} \varphi_b(x_1) \int dx_2 \overline{\varphi_b(x_2)} \varphi_a(x_2) = \langle x^2 \rangle_{ab} \cdot 0$$

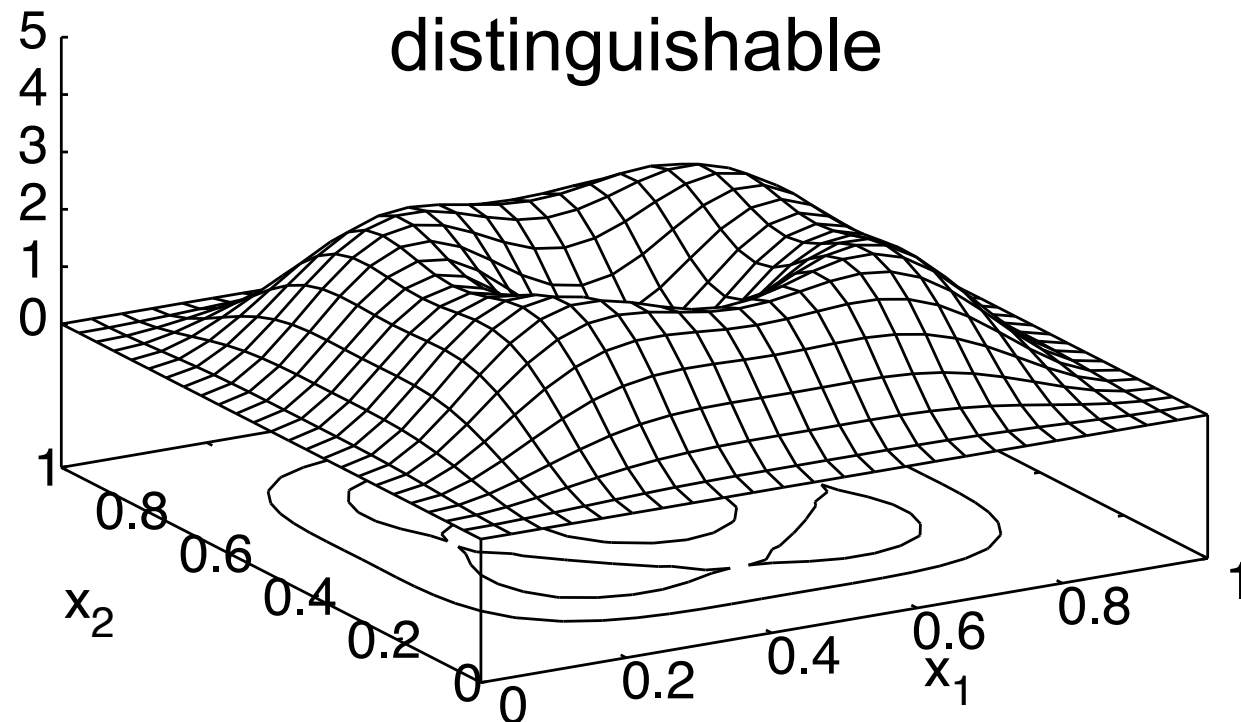
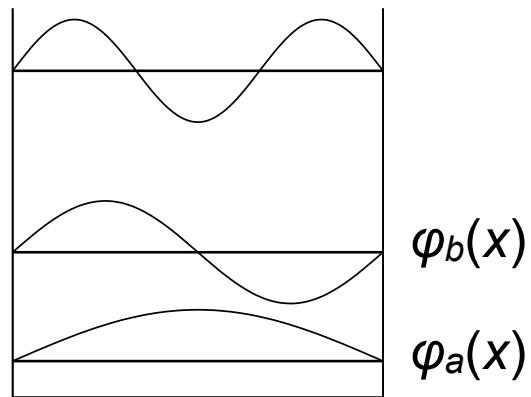
$$\langle \psi_{12} | x_2^2 | \psi_{21} \rangle = \int dx_1 \overline{\varphi_a(x_1)} \varphi_b(x_1) \int dx_2 x_2^2 \overline{\varphi_b(x_2)} \varphi_a(x_2) = 0 \cdot \langle x^2 \rangle_{ba}$$

$$\langle \psi_{12} | x_1 x_2 | \psi_{21} \rangle = \int dx_1 x_1 \overline{\varphi_a(x_1)} \varphi_b(x_1) \int dx_2 x_2 \overline{\varphi_b(x_2)} \varphi_a(x_2) = \langle x \rangle_{ab} \cdot \langle x \rangle_{ba}$$

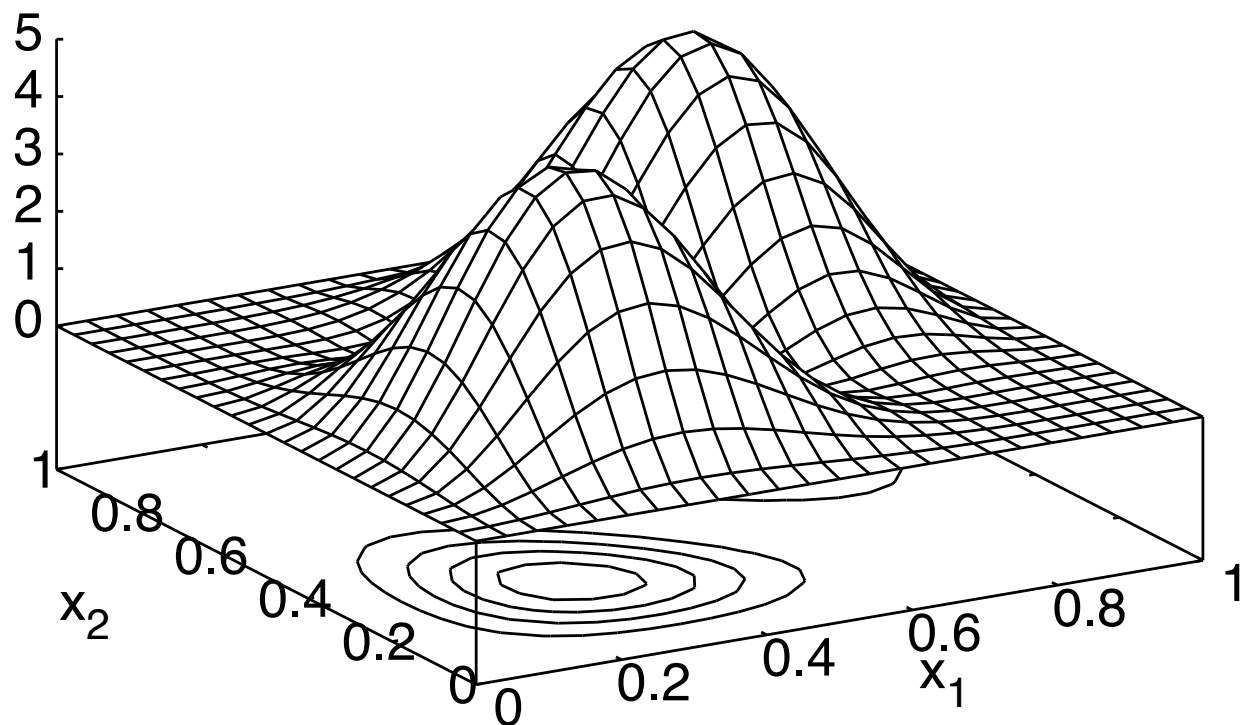
$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle \mathbf{x} \rangle_{ab}|^2$$

Bosons prefer company
Fermions keep their distance

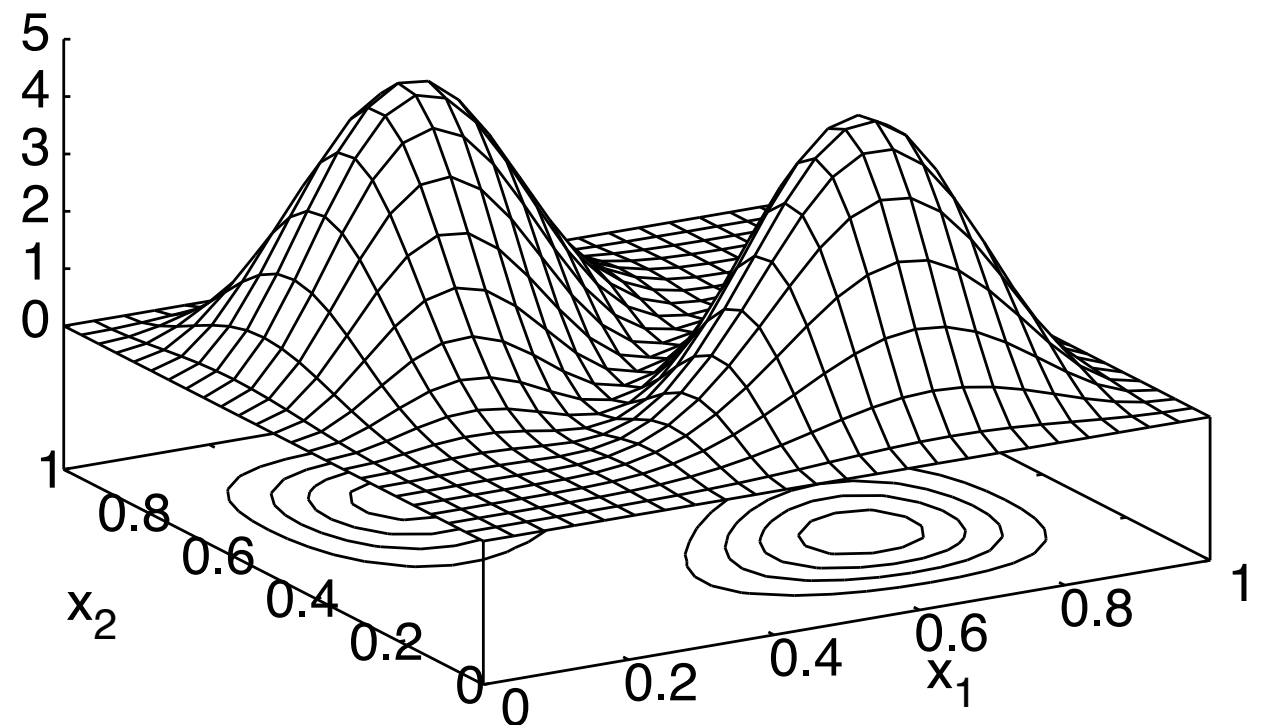
probability density for 2 particles in a box



symmetric



anti-symmetric



How about electrons on the moon?

in principle we need to antisymmetrize the wave-function for all electrons in the universe



really?

product states of states with zero overlap will not give an exchange contribution

$$\langle \psi_{12} | M | \psi_{21} \rangle = \int dx_1 dx_2 \overline{\varphi_a(x_1) \varphi_b(x_2)} M(x_1, x_2) \varphi_b(x_1) \varphi_a(x_2)$$

zero overlap makes electrons actually distinguishable by their coordinate

in practice:

can exclude electrons with negligible overlap from antisymmetrization

more practical example: **spin**

need not antisymmetrize electrons of different spin

when we are only interested in observables that do not change spin