The square potential well

Exact solution and
Variational solution using
Plane Waves and Gaussians

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Introduction

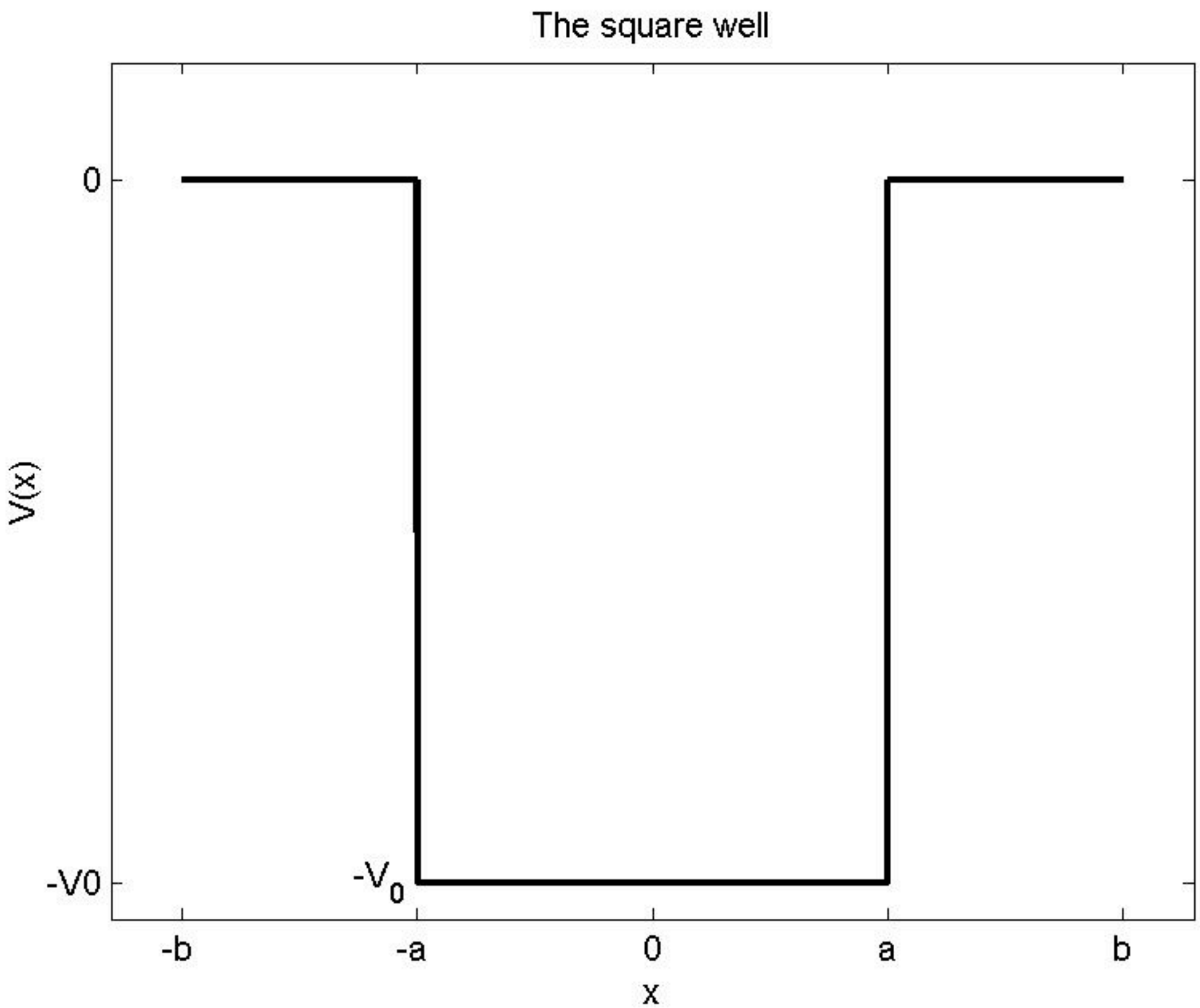
- We wish to illustrate the methods of density functional theory by going through an example in 1D, and these are the starting steps of the project.

•First Anders will present the square well and the exact solution

•Then Edda will present an approximation based on a basis set of gaussians

•Finally Egill will present an approximation using plane wave as a basis set and compare the results of these different approaches

Square Well



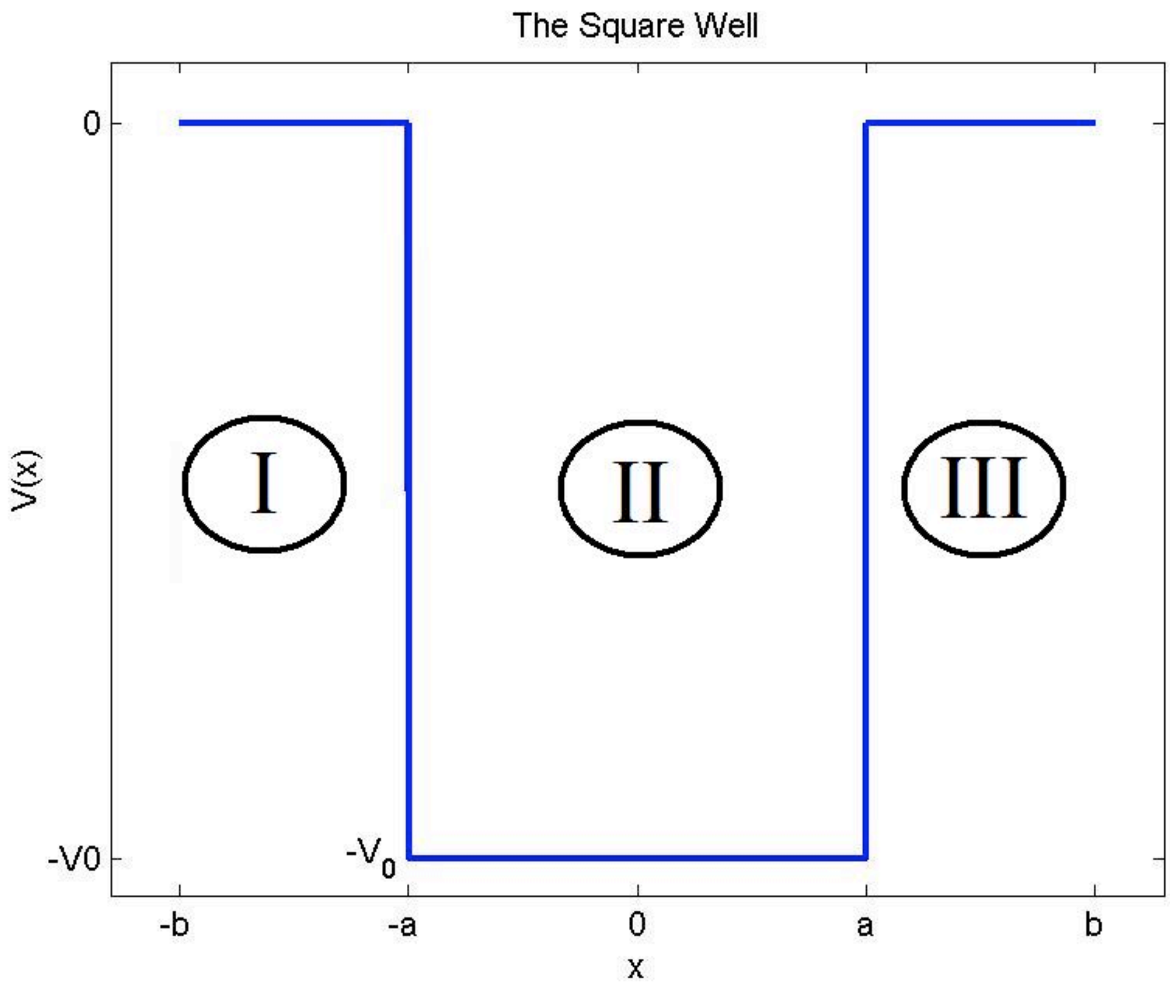
$$V(x) = \begin{cases} -V_0 & ,|x| < a \\ 0 & ,|x| > a \end{cases}$$

Case: $E < 0$

- In our approximation of the Lithium atom we are only interested in the bound states, and therefore only consider $E < 0$
- The time independent Schrödinger equation is:

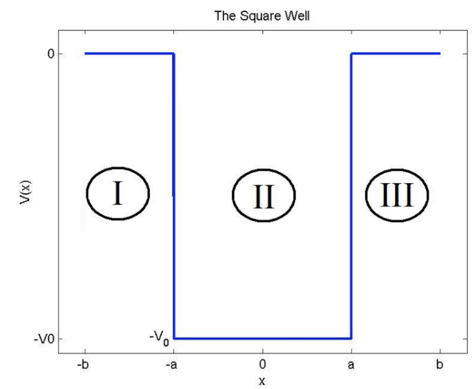
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x)\right]\psi(x) = E\psi(x)$$

Regions



Region I and III

$$a < |x|$$



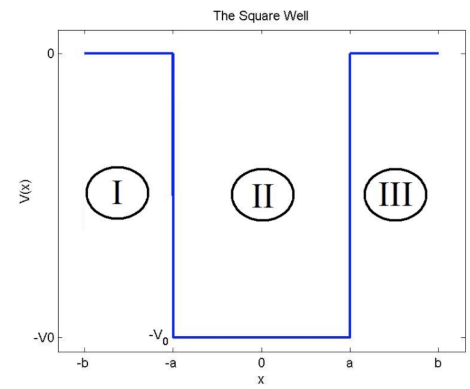
$$\left[-\frac{\hbar^2}{2m}\nabla^2\right]\psi(x) = E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) = \beta^2\psi(x)$$

$$\beta = \sqrt{-\frac{2mE}{\hbar^2}} = \sqrt{\frac{2m|E|}{\hbar^2}}$$

Region II

$$|x| < a$$



$$\left[-\frac{\hbar^2}{2m}\nabla^2 - V_0\right]\psi(x) = E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m(E+V_0)}{\hbar^2}\psi(x) = \alpha^2\psi(x)$$

$$\alpha = \sqrt{\frac{2m(V_0 - |E|)}{\hbar^2}}$$

The even solutions

$$\psi(x) = A\cos(\alpha x) \qquad 0 < x < a$$

$$\psi(x) = Ce^{-\beta x} \qquad x > a$$

- By matching up the wavefunctions at the boundaries $x = \pm a$ gives:

$$A\cos(\alpha a) = Ce^{-\beta a}$$

$$-\alpha\sin(\alpha a) = -\beta Ce^{-\beta a}$$

- Which leads to the equation:

$$\alpha\tan(\alpha a) = \beta$$

The odd solutions

$$\psi(x) = B\sin(\alpha x) \qquad 0 < x < a$$

$$\psi(x) = Ce^{-\beta x} \qquad x > a$$

•By matching up the wavefunctions at the boundaries $x = \pm a$ gives:

$$A\cos(\alpha a) = Ce^{-\beta a}$$

$$-\alpha\sin(\alpha a) = -\beta Ce^{-\beta a}$$

•Which leads to the equation:

$$\alpha\cot(\alpha a) = -\beta$$

Energy Levels

- The energy levels of the bound states are found by solving the transcendental equations, either numerically or graphically
- We introduce the dimensionless quantities:

$$\xi = \alpha a \quad \text{and} \quad \eta = \beta a$$

- Giving the equations

$$\xi \tan \xi = \eta \qquad \text{(for even states)}$$

$$\xi \cot \xi = -\eta \qquad \text{(for odd states)}$$

Energy Levels

- Note that both ξ and η must be positive and such that:

  $$\xi^2 + \eta^2 = \gamma^2$$

  where

  $$\gamma = \sqrt{\frac{2mV_0a^2}{\hbar^2}}$$

  γ is often referred to as the strength parameter

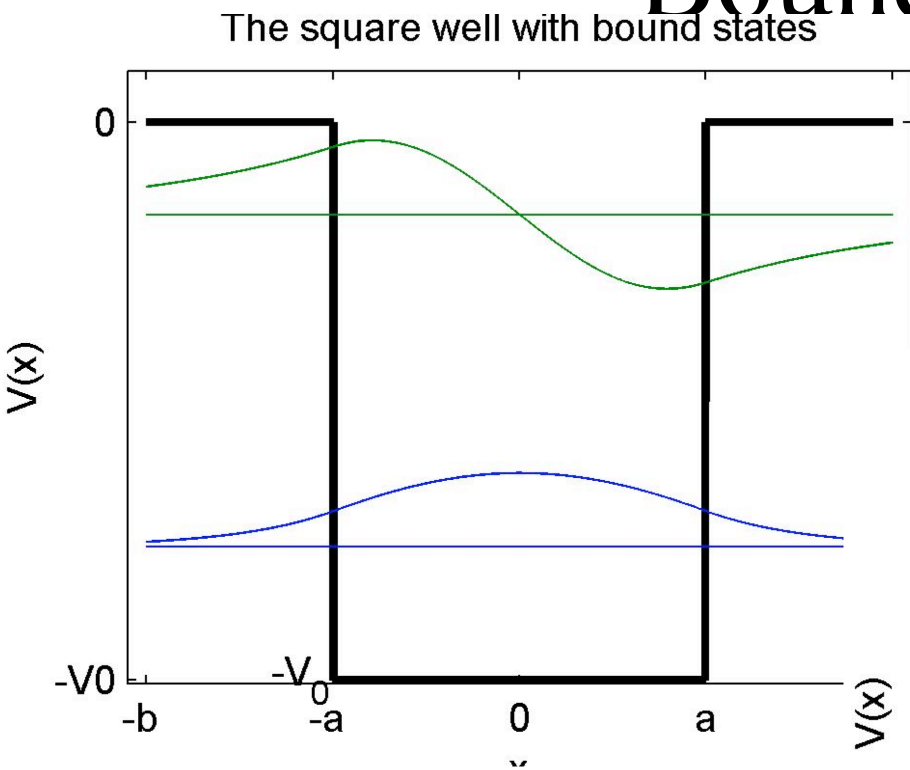
Numerical solution

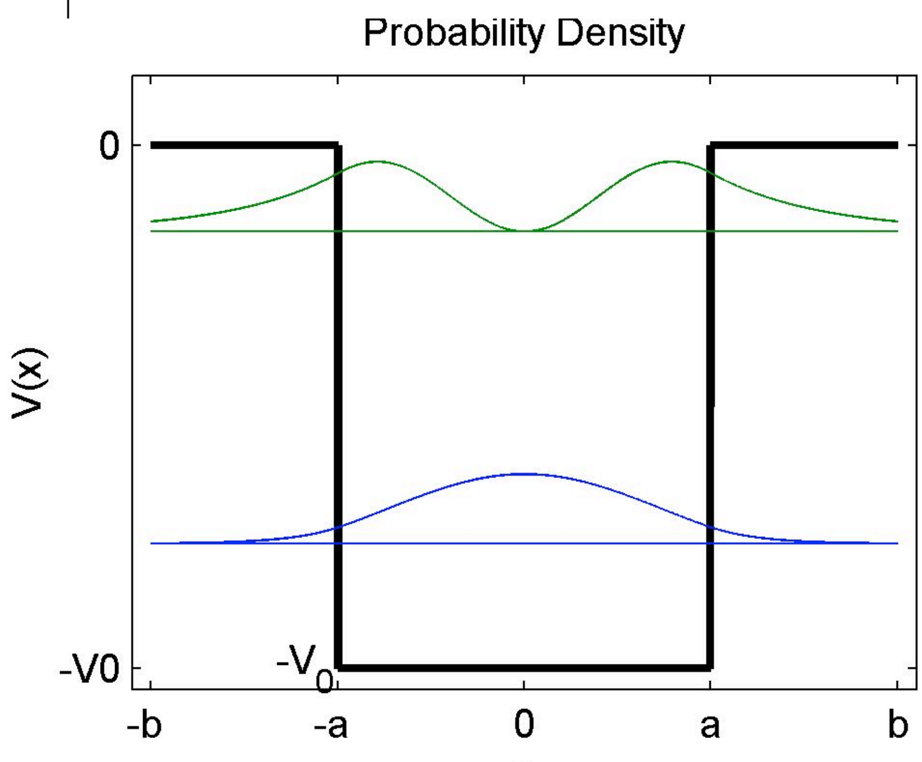
- The equation $\xi^2 + \eta^2 = \gamma^2$ is solved numerically

Results

- Using a=1.55Å and that the ground state energy should be equal to the ionization energy –5.7eV I get by trial and error that V0=7.51eV.

Bound states:





Strength parameter

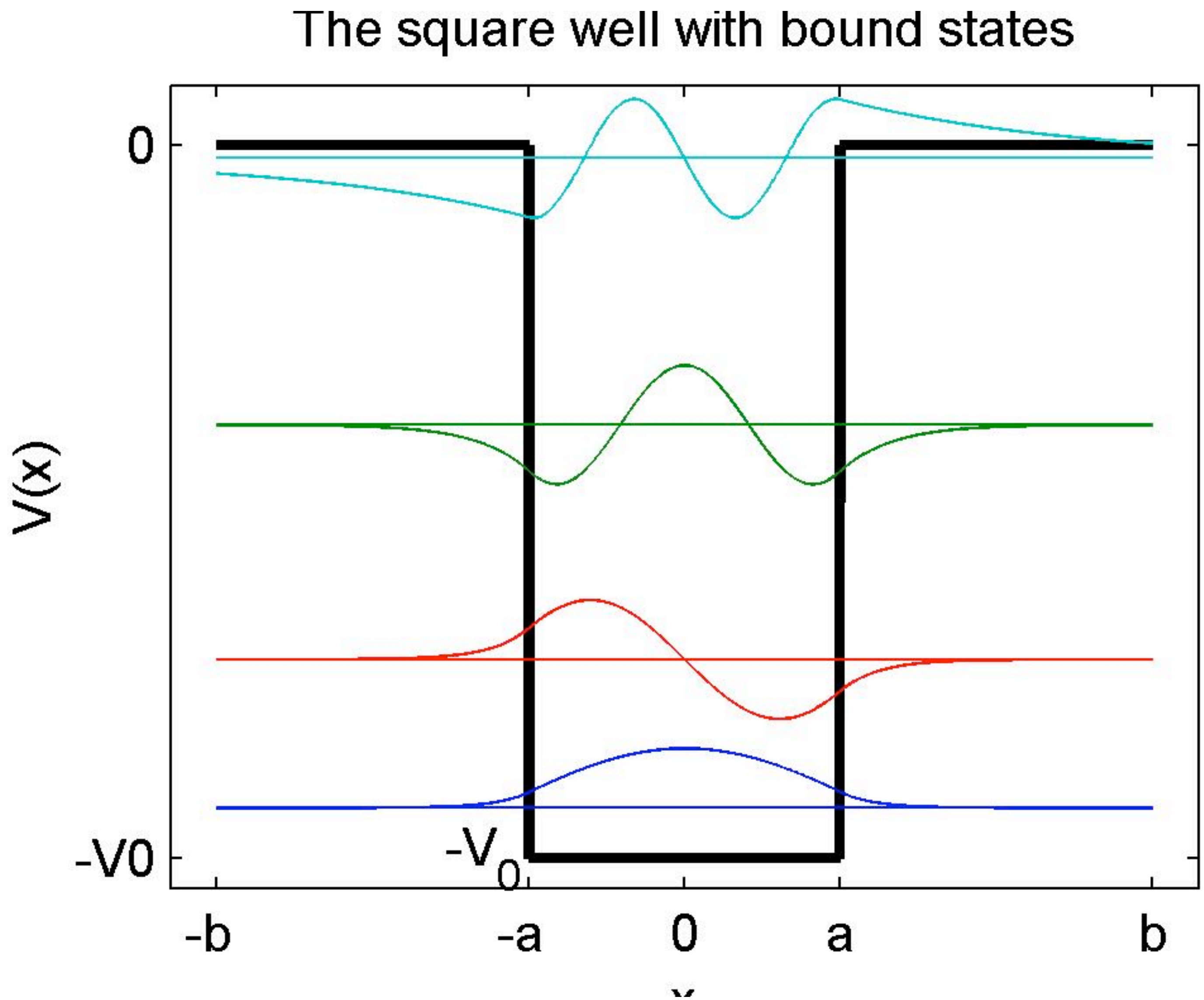
$$\gamma = \sqrt{\frac{2mV_0a^2}{\hbar^2}}$$

- The number of bound states increases as a function of the strength parameter, and assuming constant mass, the combination

  $$V_0a^2$$

  is the important parameter, determining the number of bound states, however not in a linier fashion.

Increasing V_0



Increasing *a*