Variational Calculations in 1D Square Well using Plane Waves Basis Set

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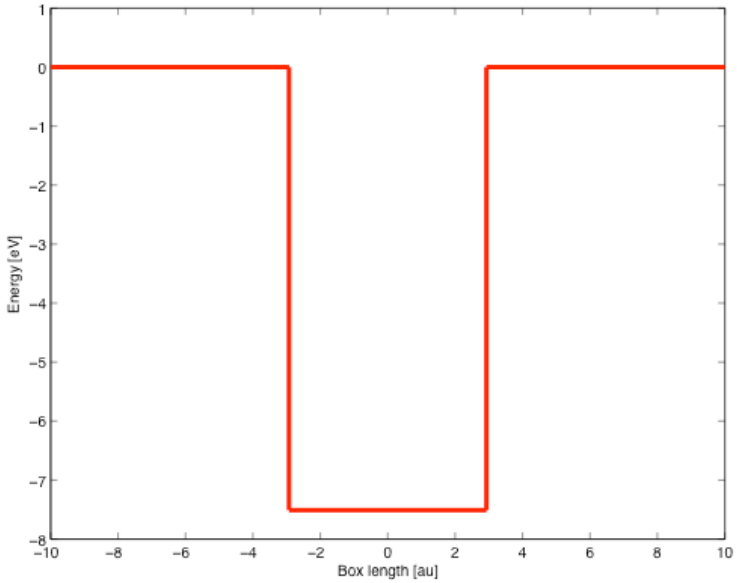
The Problem

- Calculate the bound state energies, wave functions and probability functions of a particle in a 1D square potential using plane waves as a basis set.

$$V = \begin{cases} 0 & -b \le x < -a, \qquad a < x \le b \\ V_0 & -a \le x \le a \end{cases}$$



- This simple potential could possible approximate the core of an atom with one valence electron, e.g. the Li atom.
- We use the Li atomic radius (a); 2.93 bohr.
- We set the depth of the well (V_0) at ~7.51 eV which gives the desired ground state energy for the Li atom; ca. -5.7 eV.

Variational Calculations

The trial function:

$$\phi = \frac{c_0}{\sqrt{2b}} + \sum_{n=1}^{k} c_n \frac{1}{\sqrt{b}} \cos\left(\frac{n\pi x}{b}\right) + \sum_{n=1}^{k} d_n \frac{1}{\sqrt{b}} \sin\left(\frac{n\pi x}{b}\right) \qquad (1)$$

A trial function that depends linearly on the variational parameters leads to a secular determinant:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{21} - ES_{21} & \cdots & H_{k1} - ES_{k1} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & & H_{k2} - ES_{k2} \\ \vdots & \vdots & & \vdots \\ H_{1k} - ES_{1k} & H_{2k} - ES_{2k} & \cdots & H_{kk} - ES_{kk} \end{vmatrix} = 0$$

$$H_{ij} = \int \phi_i \hat{H} \phi_j \, dx \qquad S_{ij} = S_{ji} = \int \phi_i \phi_j \, dx = \delta_{ij}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_{pot}$$

$\hat{H}$ is Hermitian: $H_{ij} = H_{ji}$

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The secular determinant simplifies if the trial function is a linear combination of orthonormal functions:

$$\begin{vmatrix} H_{11} - E & H_{21} & \cdots & H_{k1} \\ H_{12} & H_{22} - E & \cdots & H_{k2} \\ \vdots & \vdots & & \vdots \\ H_{1k} & H_{2k} & \cdots & H_{kk} - E \end{vmatrix} = 0$$

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Ground State Energy Convergence

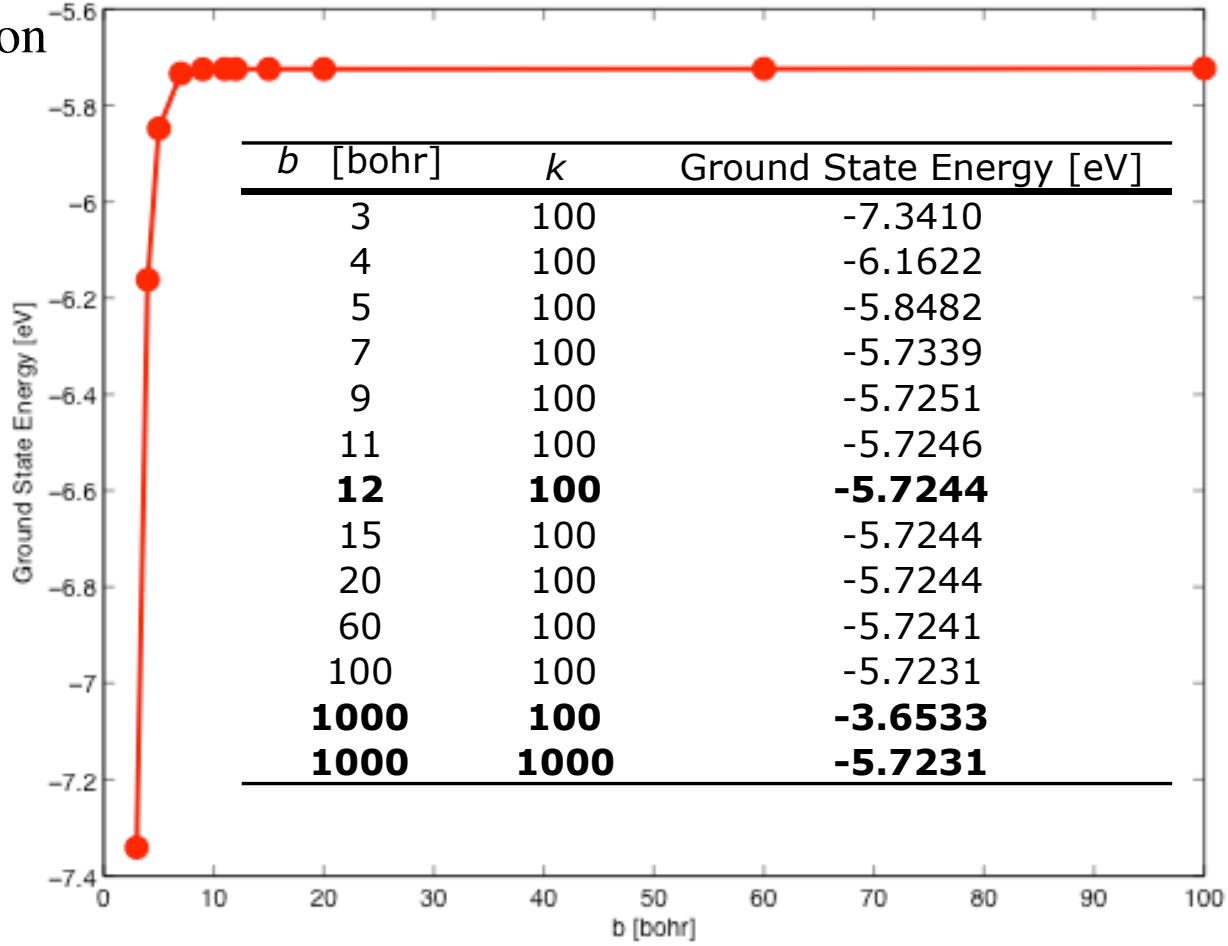
The Separation Between Wells

$$\phi = \frac{c_0}{\sqrt{2b}} + \sum_{n=1}^{k} c_n \frac{1}{\sqrt{b}} \cos\left(\frac{n\pi x}{b}\right) + \sum_{n=1}^{k} d_n \frac{1}{\sqrt{b}} \sin\left(\frac{n\pi x}{b}\right) \qquad (1)$$

The length b ($2b$ is the separation between adjacent wells) is chosen to be 12 bohr units so it converges at the exact value -5.7244 eV. k is constrained to 100 or 1000 in eq. (1).

When the wells are closer together the energy is lower because of the formation of chemical bonds.

When the separation becomes greater, more plane waves are necessary for an accurate approximation.



b [bohr]	k	Ground State Energy [eV]
3	100	-7.3410
4	100	-6.1622
5	100	-5.8482
7	100	-5.7339
9	100	-5.7251
11	100	-5.7246
12	**100**	**-5.7244**
15	100	-5.7244
20	100	-5.7244
60	100	-5.7241
100	100	-5.7231
1000	**100**	**-3.6533**
1000	**1000**	**-5.7231**

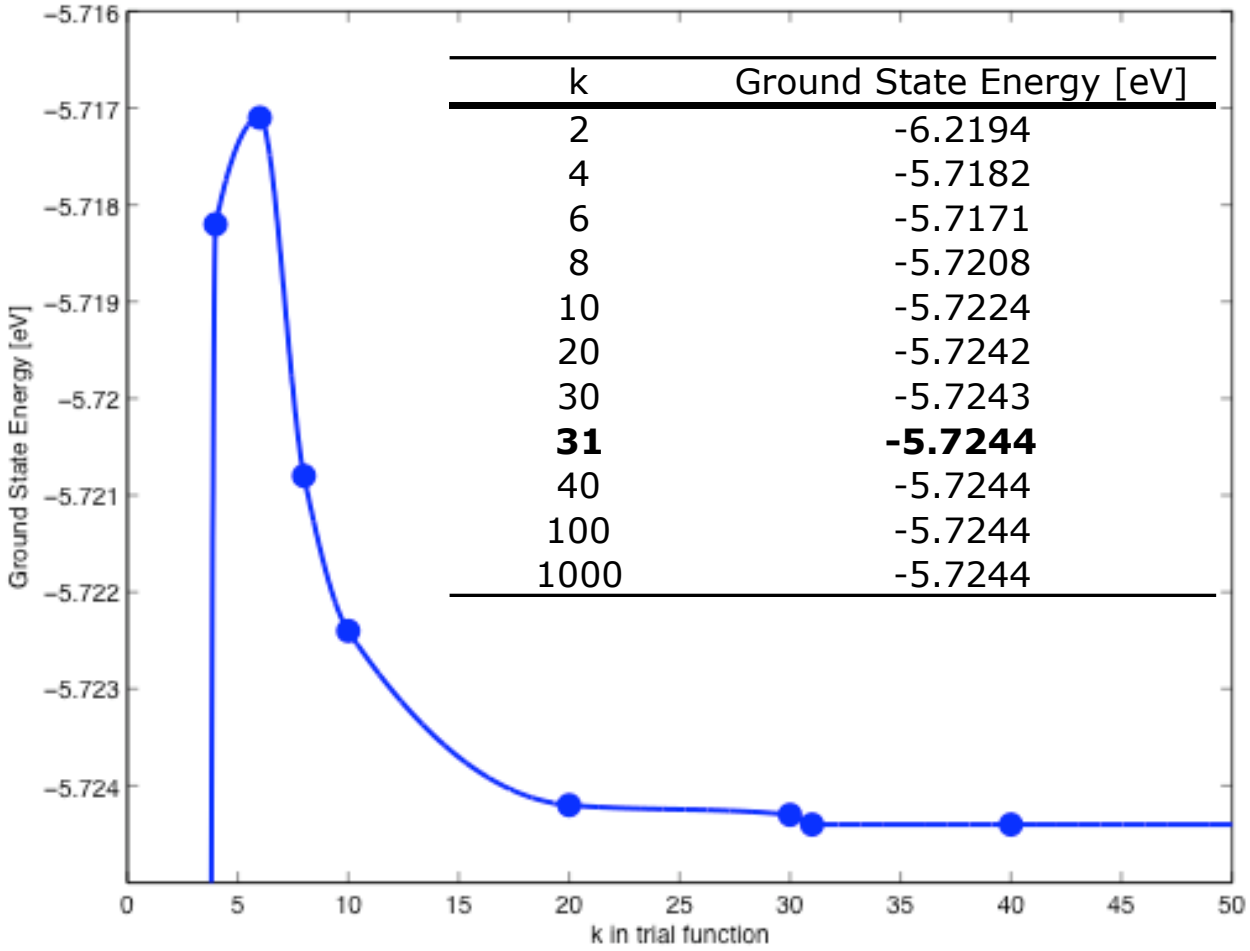
Ground State Energy Convergence

Number of Plane Waves

$$\phi = \frac{c_0}{\sqrt{2b}} + \sum_{n=1}^{k} c_n \frac{1}{\sqrt{b}} \cos\left(\frac{n\pi x}{b}\right) + \sum_{n=1}^{k} d_n \frac{1}{\sqrt{b}} \sin\left(\frac{n\pi x}{b}\right) \qquad (1)$$

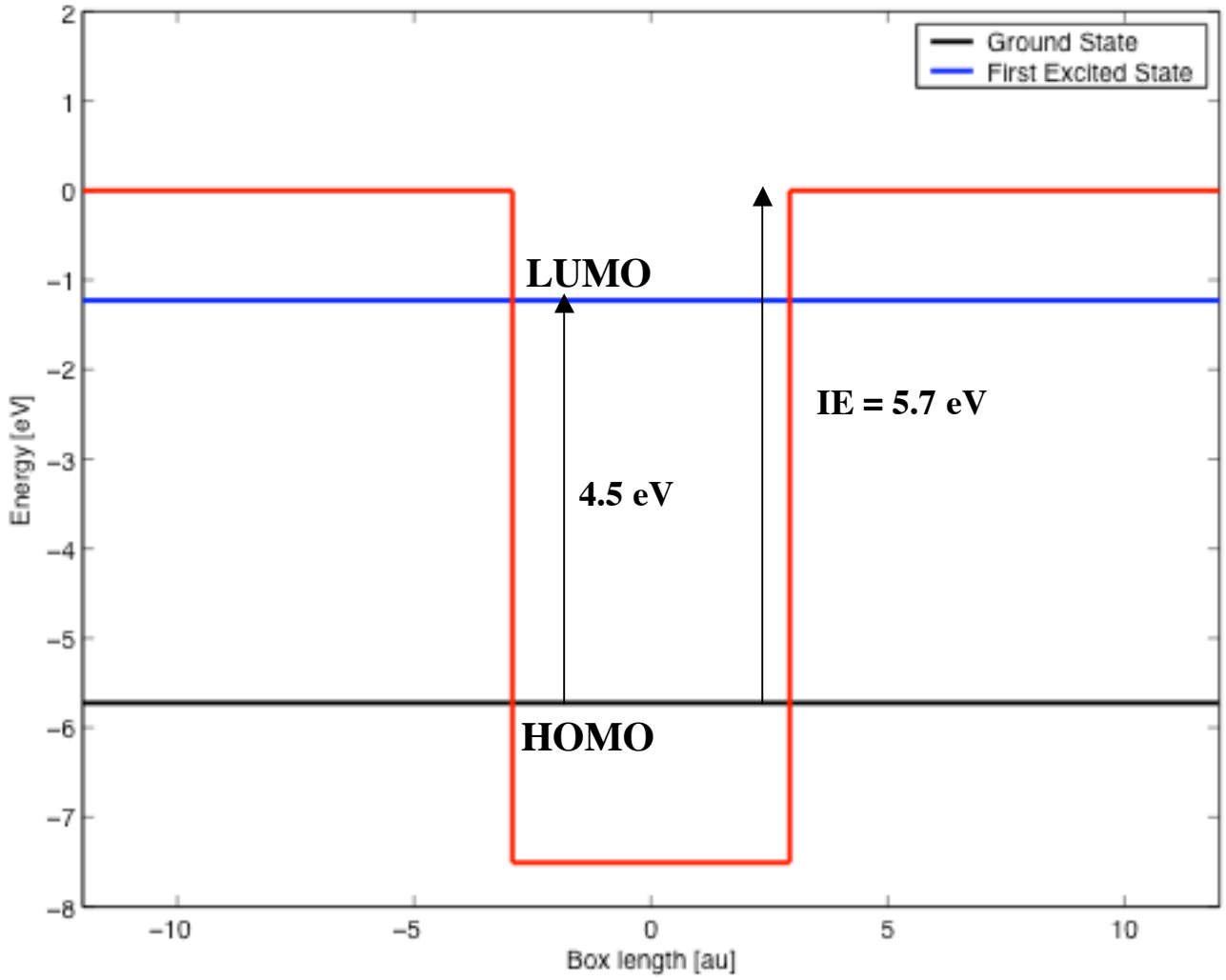
The index *k* in eq. (1) is chosen to be 31 so it converges to the exact solution. *b* is constrained at 12 bohr units.

Adding additional plane waves to the trial function does not change the ground state energy value to 4 decimal digits.

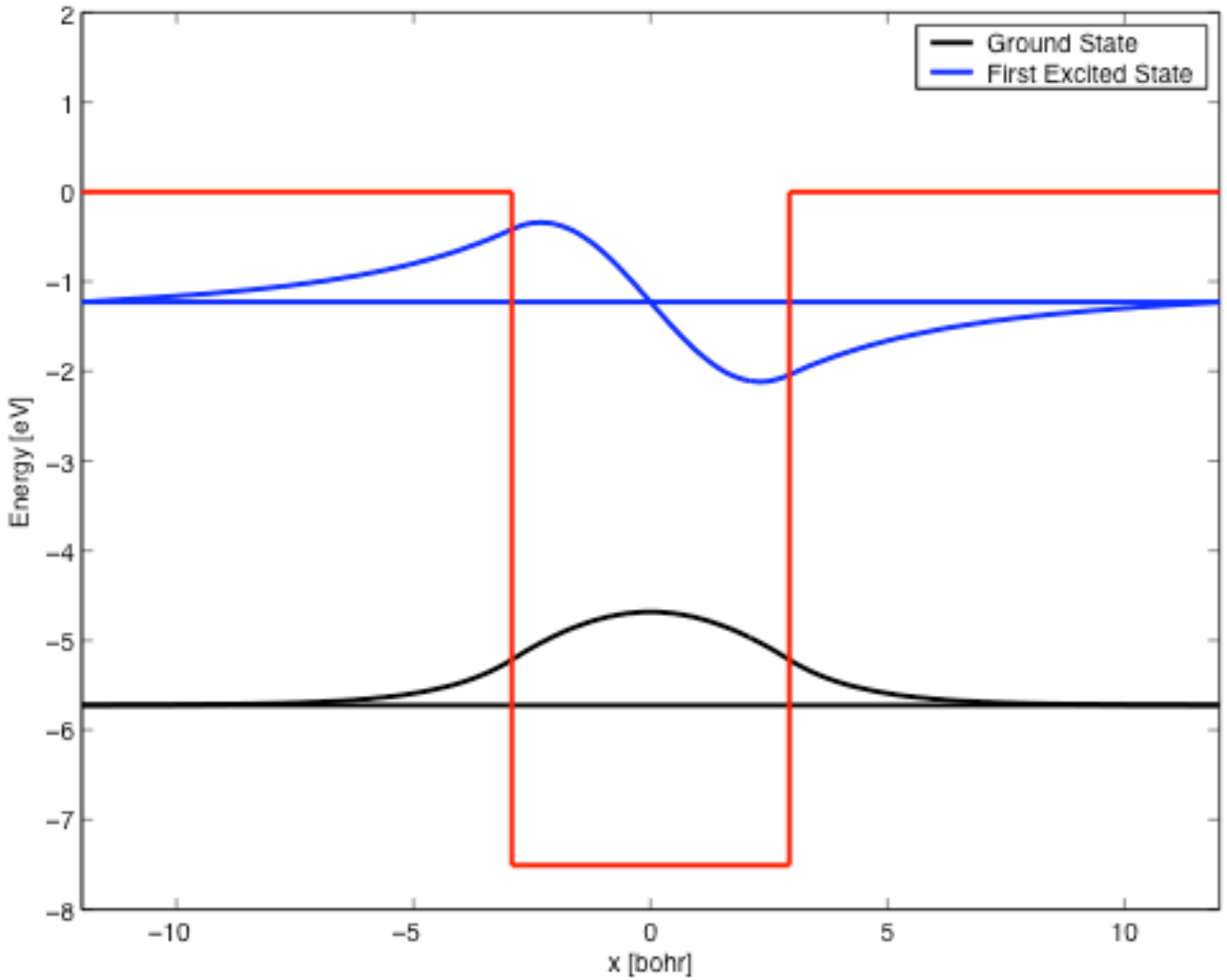


k	Ground State Energy [eV]
2	-6.2194
4	-5.7182
6	-5.7171
8	-5.7208
10	-5.7224
20	-5.7242
30	-5.7243
31	**-5.7244**
40	-5.7244
100	-5.7244
1000	-5.7244

The energy levels of a particle in a square well

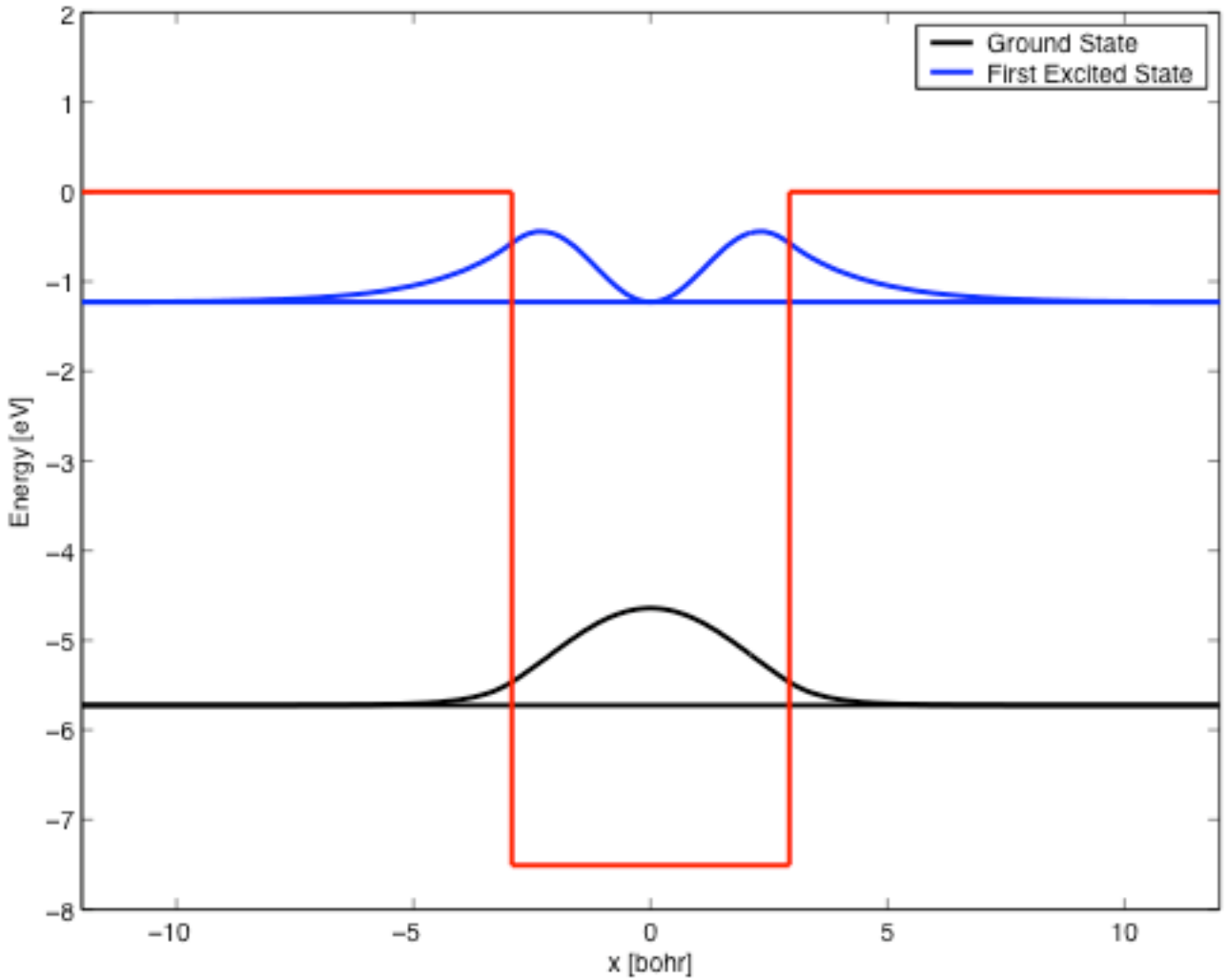


The wave functions of a particle in a square well



wave function = eigenvector • trial function

The probability functions of a particle in a square well



probability function = | wave function |^2

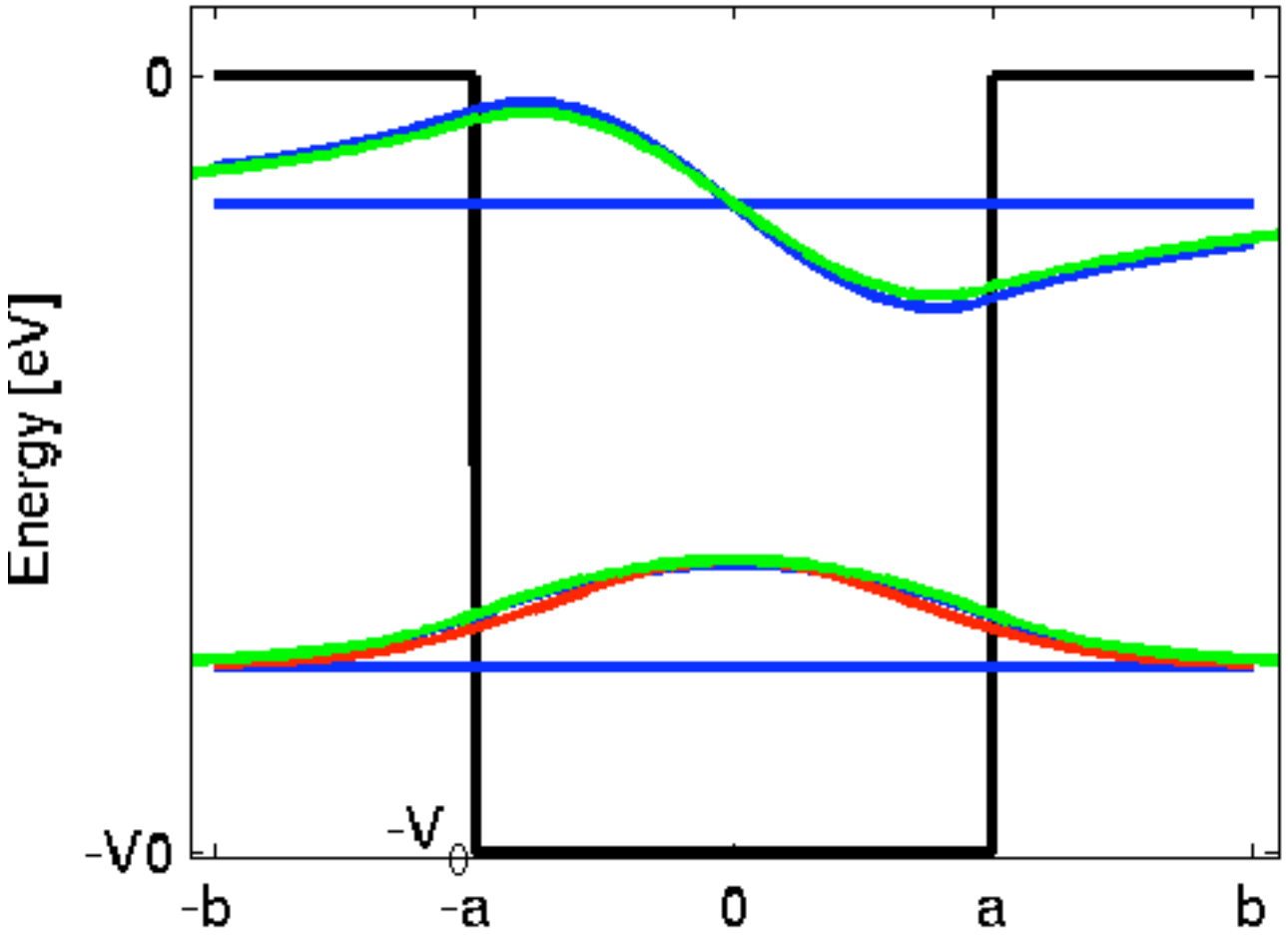
The Difference in Ground State Energy Levels

Method	Ground State Energy [eV]	Difference [eV]
Exact	-5.7244	-
3 Gaussians*	-5.7128	0.01
31 Plane waves**	-5.7244	0.0000

*** Adding more gaussians to the basis set would lead to better convergence in the ground state energy.**

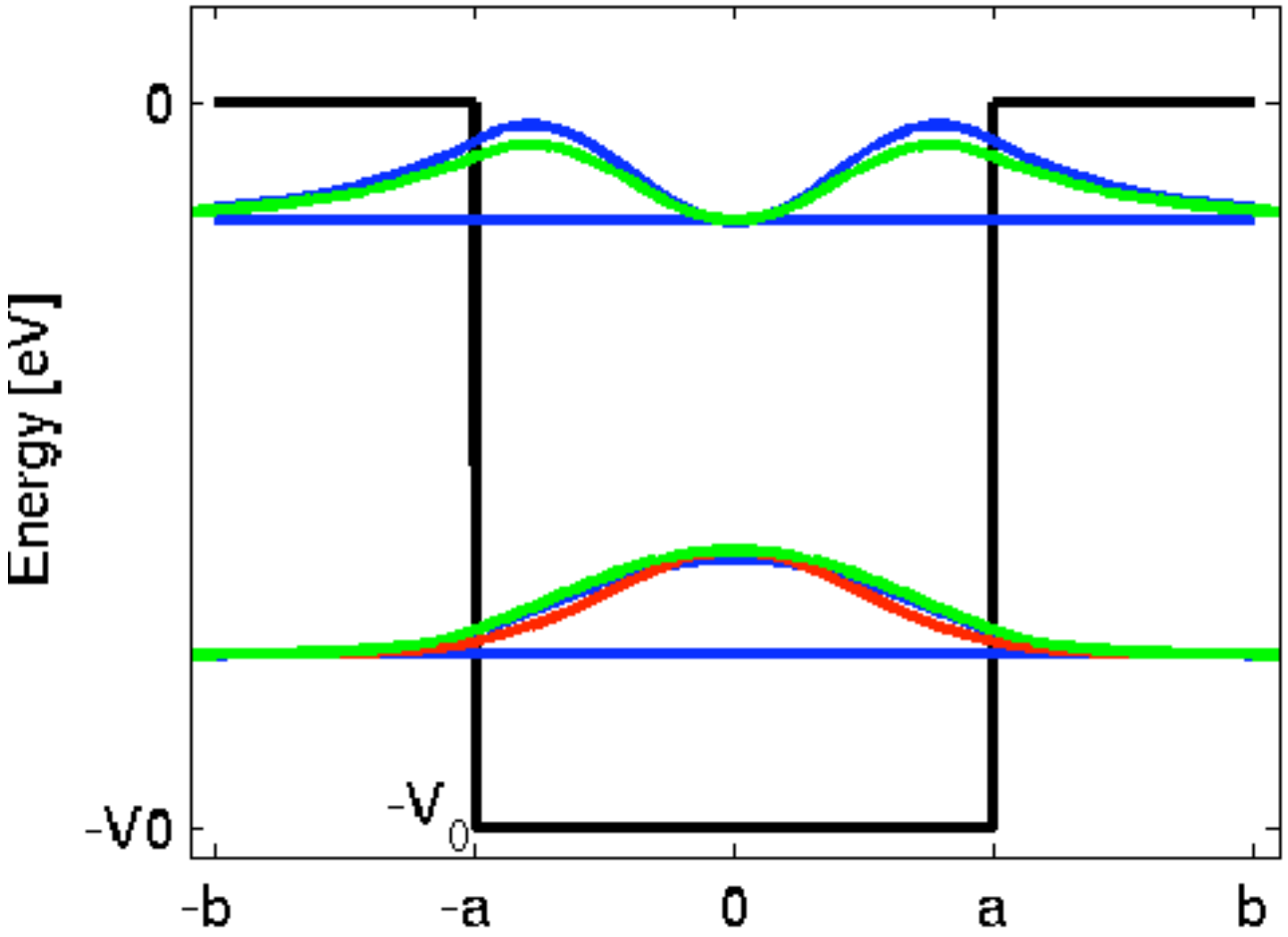
**** The index *k* in the trial function is equal to 31 so this value is calculated from 31 cosines functions and one constant term. The sinus functions do not contribute in the ground state energy level because they are odd functions.**

The wave functions of a particle in a square well



Exact
3 Gaussians
31 Plane Waves

The probability functions of a particle in a square well



Exact
3 Gaussians
31 Plane Waves

Conclusions

- The ground state energy from the variational calculations converges to the exact solution if we have complete basis set. One would have to add more terms to the gaussian basis set to make it complete.
- The wave functions and the probability functions from the gaussian basis set and the plane waves match the exact functions.

Further Implementations

- Calculate the bond energy between two Li atoms.
- Include more terms in the Hamiltonian, e.g.
  - Interactions between two electrons:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_{pot} + \frac{1}{|r_1 - r_2|}$$

  - External electric potential:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_{pot} - eU(x)$$