

Chemistry 3P51 – Fall 2013

Quantum Chemistry

Lecture No. 30

Nov 18th, 2013

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Objectives

- To introduce the variational method as a tool to determine approximate energies and wave-functions of quantum system.
- To apply the variational method to the particle-in-a-box system.
- To apply the variational method to the quantum harmonic oscillator.

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Variational method

The Schrödinger equation for a many-electron system cannot be solved analytically, but it can be solved approximately by various numerical methods. The most important of these is the **variation method**.

The variation method is based on the following theorem.

Theorem: If \hat{H} is the Hamiltonian for the system of interest, E_{exact} is the **exact** ground-state energy, and ψ is an *approximate* (“trial”) wave function, then

$$\langle E \rangle \equiv \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \geq E_{\text{exact}}$$

$d\tau$ stands for a differential volume element involving all spatial and spin coordinates of ψ

The denominator is included to normalize the trial wave function.

If ψ is the exact ground-state eigenfunction of \hat{H} , then $\langle E \rangle = E_{\text{exact}}$.
Any approximate wavefunction yields an energy that is higher than E_{exact} .

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How the variational method works

When the true eigenfunction is not known, we devise a **trial wave function** with some adjustable (“variational”) parameters

$$\psi = \psi(1, 2, \dots, N; c_1, c_2, \dots, c_n)$$

The average energy depends on the choice of these parameters, so we treat it as a function of c_i :

$$\langle E \rangle(c_1, c_2, \dots, c_n) = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$$

Next we minimize this expression with respect to the c_i 's.

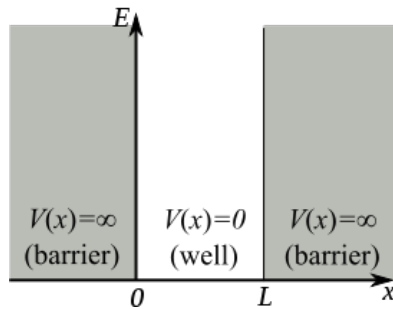
The optimal values of the parameters are obtained by solving the simultaneous equations

$$\frac{\partial \langle E \rangle}{\partial c_i} = 0, \quad i = 1, 2, \dots, n$$

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Example of the variational method: Reminder on the particle-in-a-box system

We have previously studied the particle-in-a-box system. We will consider this system only for the purposes of showing how the variational method is applied.



$$V(x) = \begin{cases} 0 & ; \quad 0 \leq x \leq L \\ +\infty & ; \quad \text{otherwise} \end{cases}$$

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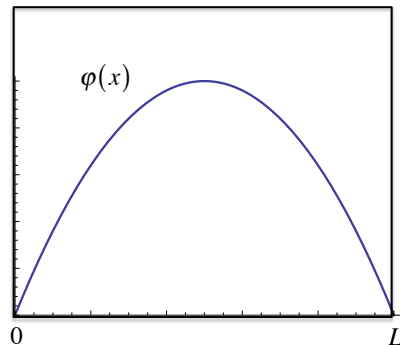
Test wave-function for the particle-in-a-box system

The test function we use for the system must be **well-behaved** and should also be consistent with the **boundary conditions** imposed by the potential.

In order to satisfy the boundary conditions $\varphi(0) = 0 = \varphi(L)$

Thus, we propose

$$\varphi(x) = \begin{cases} x(L-x) & ; \quad 0 \leq x \leq L \\ 0 & ; \quad \text{otherwise} \end{cases}$$



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Computing the expected value of energy for the test wave-function

In order to apply the variational method we compute the following integrals:

$$\int_0^L \varphi^*(x) \varphi(x) dx = \frac{L^5}{30}$$

$$\int_0^L \varphi^*(x) \hat{H} \varphi(x) dx = -\frac{\hbar^2}{2m} \int_0^L \varphi^*(x) \varphi''(x) dx = \frac{\hbar^2 L^3}{6m}$$

from where we obtain the **variational energy**

$$\langle E \rangle_\varphi = \frac{\int_0^L \varphi^*(x) \hat{H} \varphi(x) dx}{\int_0^L \varphi^*(x) \varphi(x) dx} = \frac{5\hbar^2}{mL^2}$$

Comparing the variational energy with the actual energy for a particle in a box

Let us compare the recently computed ground-state **variational energy** with the **actual ground-state energy of the system**

$$\langle E \rangle_\varphi = \frac{5\hbar^2}{mL^2} \Rightarrow \text{Error} \sim 1.32 \%$$

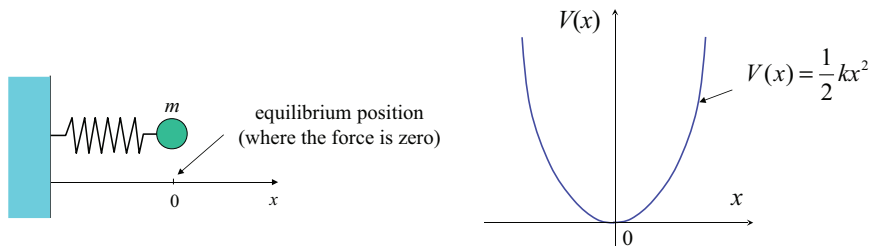
$$E_{\text{g.s}}^{\text{actual}} = \frac{\pi^2 \hbar^2}{2mL^2}$$

It is important to notice that:

- The **variational energy** is **greater than** the **actual energy**, as stated when we presented the variational method.
- The “test” wave-function possesses properties related with the system. In this case, boundary conditions and no nodes (ground state)

Example of the variational method: Reminder on the quantum harmonic oscillator

We have previously studied the quantum harmonic oscillator. We will consider this system only for the purposes of showing how the variational method is applied.



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Test wave-function for the quantum harmonic oscillator

The test function we use for the system must be **well-behaved** and should also be consistent with the **boundary conditions** imposed by the potential.

Thus, we propose $\varphi(x) = e^{-ax^2}$

Notice that in this case, unlike the wave-function used for a particle in a box (see lecture 30), our test wave-function has a **parameter**, a

Such a **parameter** is going to play a key role in our example, as we will see soon.

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Computing the expected value of energy for the test wave-function

In order to apply the variational method we compute the following integrals:

$$\begin{aligned}\int_{-\infty}^{\infty} \varphi^*(x) \varphi(x) dx &= \sqrt{\frac{\pi}{2a}} \\ \int_{-\infty}^{\infty} \varphi^*(x) \hat{H} \varphi(x) dx &= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \varphi^*(x) \varphi''(x) dx + \frac{1}{2} k \int_{-\infty}^{\infty} \varphi^*(x) x^2 \varphi(x) dx \\ &= \frac{\hbar^2}{2m} \sqrt{\frac{\pi}{2a}} + \frac{k}{8a^{3/2}} \sqrt{\frac{\pi}{2}}\end{aligned}$$

from where we obtain the **variational energy**

$$\langle E \rangle_{\varphi} = \frac{\int_{-\infty}^{\infty} \varphi^*(x) \hat{H} \varphi(x) dx}{\int_{-\infty}^{\infty} \varphi^*(x) \varphi(x) dx} = \frac{a\hbar^2}{2m} + \frac{k}{8a}$$

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Minimizing the variational energy with respect the test wave-function's parameter

Let us recall that the **variational energy** is greater than or equal to the actual energy.

Since our **variational energy** depends on **a**, and the stated inequality is true for any value of **a**, we minimize the energy to make it as close the actual energy as possible

$$\begin{aligned}\langle E \rangle_{\varphi} &= \frac{a\hbar^2}{2m} + \frac{k}{8a} & \frac{\partial \langle E \rangle_{\varphi}}{\partial a} = 0 &\Rightarrow \frac{\hbar^2}{2m} - \frac{k}{8a^2} = 0 \Rightarrow \\ a_1 &= +\frac{\sqrt{mk}}{2\hbar} \\ a_2 &= -\frac{\sqrt{mk}}{2\hbar}\end{aligned}$$

Since the test wave-function should be normalizable, we neglect the **negative solution for a**. Thus, the **acceptable value of the parameter a is**

$$a_1 = +\frac{\sqrt{mk}}{2\hbar}$$

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Comparing the variational energy with the actual energy for the quantum harmonic oscillator

Let us compare the recently computed ground-state **variational energy** with the **actual ground-state energy of the system**.

Substituting the **recently value of a** in the **variational energy** we obtain

$$\langle E \rangle_{\varphi} \Big|_{a=a_1=\frac{\sqrt{mk}}{2\hbar}} = \frac{1}{4}\hbar\sqrt{\frac{k}{m}} + \frac{1}{4}\hbar\sqrt{\frac{k}{m}} = \frac{1}{2}\hbar\omega$$

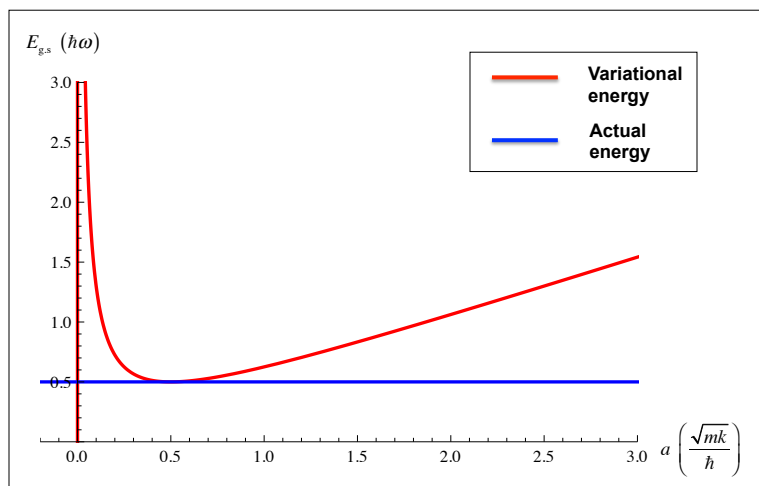
$$\langle E \rangle_{\varphi}^{\min} = \frac{1}{2}\hbar\omega \quad \Rightarrow \text{Error} = 0.00 \%$$

$$E_{\text{g.s}}^{\text{actual}} = \frac{1}{2}\hbar\omega \quad \textbf{Exact!}$$

Important. The test wave-function that results for the found value of a , coincides with the actual ground-state wave-function.

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Graph of the variational energy and exact ground-state energies for different values of a



The **variational energy** is always greater than or equal to the **actual energy** for any value of the parameter a

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