Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 31
Nov 20th, 2013

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Objectives

- To remind the student how the variational principle works
- To introduce the linear variational method
- To apply the linear variational method to a particle in a box

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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

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

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

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

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

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

The linear variational method

- As mentioned during lectures, we can test several wave-functions for one single system.
- Of particular interest it will be to consider a test function of the following form

$$\boxed{\varphi = c_1 f_1 + c_2 f_2 + \ldots + c_n f_n}$$

- That is, the test function is constructed as a **linear combination** of *n* different known functions $\{f_1, f_2, f_3, \ldots f_n\}$
- The coefficients $\{c_1, c_2, c_3, \ldots, c_n\}$ are constants to be determined by the variational method

System of linear equations for the variational method

- When the variational method is applied to the function presented in the previous slide, the following **system of linear equations** is obtained

$$\begin{bmatrix} S_{11}W-H_{11} & S_{12}W-H_{12} & \cdots & S_{1n}W-H_{1n} \\ S_{21}W-H_{21} & S_{22}W-H_{22} & \cdots & S_{2n}W-H_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ S_{n1}W-H_{n1} & S_{n2}W-H_{n2} & \cdots & S_{nn}W-H_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ . \\ . \\ c_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ . \\ . \\ 0 \end{bmatrix}$$

- In this equation:

$$W - \text{ Variational integral (energies)}$$

$$S_{ij} = \int f_i^* f_j \, d\tau \quad \text{Overlap} \qquad \begin{matrix} i = 1,2,..,n \\ j = 1,2,..,n \end{matrix}$$

$$H_{ij} = \int f_i^* \hat{H} f_j \, d\tau \quad \text{Hamiltonian matrix}$$

where we have symbolically represented three-dimensional integrals.

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The secular equation

- It should be kept in mind that the objective of the variational method is to determine the energies *W* as well as the coefficients $\{c_1,c_2,c_3,\ldots,c_n\}$
- A test wave-function like the one shown in the slide 4 will lead, in general, to *n* different energies $\{W_1,W_2,W_3,\ldots,W_n\}$; each of them with their corresponding *c's* coefficients.
- Since we are looking for **non-trivial solutions** (solutions for which the coefficients *c's* are different from zero), the **determinant** of the **matrix of coefficients** must be zero. That is

$$\boxed{\begin{vmatrix} S_{11}W-H_{11} & S_{12}W-H_{12} & \cdots & S_{1n}W-H_{1n} \\ S_{21}W-H_{21} & S_{22}W-H_{22} & \cdots & S_{2n}W-H_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ S_{n1}W-H_{n1} & S_{n2}W-H_{n2} & \cdots & S_{nn}W-H_{nn} \end{vmatrix} = 0}$$

- This equation is known as the **secular equation**.

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Solutions of the secular equation

- The determinant previously shown will lead to a **polynomial of degree *n***, which will have in general ***n* different solutions**.

- The *n* different energies $\{W_1, W_2, W_3, \ldots, W_n\}$, when sorted out from the smallest to greatest value, say $W_1 < W_2 < W_3 < \ldots < W_n$ **represent approximations to the first *n* energies of the system**

- For each value of *W*, a **set of coefficients** should be determined. Each of these sets of coefficients will provide the corresponding **approximate wave-functions for the first *n* states of the system**.

$$
\begin{array}{l}
W_1 \to c_{11}, c_{12,\ldots}, c_{1n} \to \varphi_1 \\
W_2 \to c_{21}, c_{22,\ldots}, c_{2n} \to \varphi_2 \\
\ldots \qquad \ldots\ldots\ldots\ldots \qquad \ldots \\
W_n \to c_{n1}, c_{n2,\ldots}, c_{nn} \to \varphi_n
\end{array}
$$

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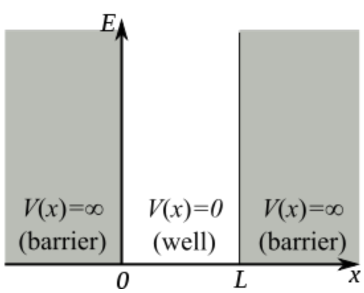
Example: Linear variational method applied to a particle in a box

- Consider once again a particle in a box



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

- We will use the following test function

$$
\begin{aligned}
\varphi &= c_1 f_1 + c_2 f_2 \\
&= c_1 x^2 (L-x) + c_2 x (L-x)^2
\end{aligned}
\qquad 0 \le x \le L
$$

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- We compute the matrix elements needed to apply the linear variational method

$$H_{11}=\int_0^L f_1^*(x)\hat{H}f_1(x)dx=-\frac{\hbar^2}{2m}\int_0^L f_1^*(x)f_1''(x)dx=\frac{\hbar^2L^5}{15m} \qquad S_{11}=\int_0^L f_1^*(x)f_1(x)dx=\frac{L^7}{105}$$

$$H_{22}=\int_0^L f_2^*(x)\hat{H}f_2(x)dx=-\frac{\hbar^2}{2m}\int_0^L f_2^*(x)f_2''(x)dx=\frac{\hbar^2L^5}{15m} \qquad S_{22}=\int_0^L f_2^*(x)f_2(x)dx=\frac{L^7}{105}$$

$$H_{12}=\int_0^L f_1^*(x)\hat{H}f_2(x)dx=-\frac{\hbar^2}{2m}\int_0^L f_1^*(x)f_2''(x)dx=\frac{\hbar^2L^5}{60m} \qquad S_{12}=\int_0^L f_1^*(x)f_2(x)dx=\frac{L^7}{140}$$

$$H_{21}=\int_0^L f_2^*(x)\hat{H}f_1(x)dx=-\frac{\hbar^2}{2m}\int_0^L f_2^*(x)f_1''(x)dx=\frac{\hbar^2L^5}{60m} \qquad S_{21}=\int_0^L f_2^*(x)f_1(x)dx=\frac{L^7}{140}$$

- Thus, the secular equation takes the following form

$$\begin{vmatrix} S_{11}W-H_{11} & S_{12}W-H_{12} \\ S_{21}W-H_{21} & S_{22}W-H_{22} \end{vmatrix}=0\Rightarrow\begin{vmatrix} \frac{L^7}{105}W-\frac{\hbar^2L^5}{15m} & \frac{L^7}{140}W-\frac{\hbar^2L^5}{60m} \\ \frac{L^7}{140}W-\frac{\hbar^2L^5}{60m} & \frac{L^7}{105}W-\frac{\hbar^2L^5}{15m} \end{vmatrix}=0\Rightarrow\left(\frac{L^7}{105}W-\frac{\hbar^2L^5}{15m}\right)^2-\left(\frac{L^7}{140}W-\frac{\hbar^2L^5}{60m}\right)^2=0$$

$$\boxed{W_1=\frac{5\hbar^2}{mL^2} \text{ and } W_2=\frac{21\hbar^2}{mL^2}}$$

Energies from the variation method

- From the previous slide we notice that W_1 < W_2. These values correspond to **approximations** of the **ground-state energy** and **first excited state energy**, respectively.

$$E_{\text{g.s}}^{\text{var}}=\frac{5\hbar^2}{mL^2} \text{ and } E_1^{\text{var}}=\frac{21\hbar^2}{mL^2}$$

- From the exact solution of the particle-in-a-box system we have

$$E_{\text{g.s}}^{\text{actual}}=\frac{4.9348\hbar^2}{mL^2} \text{ and } E_1^{\text{actual}}=\frac{19.7392\hbar^2}{mL^2}$$

which lead to the following errors in percentage

$$\text{error(g.s)}\sim 1.32\ \% \text{ and } \text{error(1st)}\sim 6.39\ \%$$

Wave-functions from the variation method

- Recall that the **system of linear equations** that need to be solved for each value of *W* is

$$\begin{bmatrix} S_{11}W - H_{11} & S_{12}W - H_{12} \\ S_{21}W - H_{21} & S_{22}W - H_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

- For W_1. Substituting $W = W_1 = \frac{5\hbar^2}{mL^2}$ the former system of linear equations turns into

$$c_1 - c_2 = 0 \Rightarrow c_2 = c_1$$

- Substitution into the test wave-function shown in slide 8 leads to

$$\varphi(x) = c_1\left[x^2(L-x) + x(L-x)^2\right]$$

where c_1 can be determined from **normalization**. Thus

$$\boxed{\varphi(x) = \sqrt{\frac{30}{L^7}}\left[x^2(L-x) + x(L-x)^2\right]}$$

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Wave-functions from the variation method

- Recall that the **system of linear equations** that need to be solved for each value of *W* is

$$\begin{bmatrix} S_{11}W - H_{11} & S_{12}W - H_{12} \\ S_{21}W - H_{21} & S_{22}W - H_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

- For W_2. Substituting $W = W_2 = \frac{21\hbar^2}{mL^2}$ the former system of linear equations turns into

$$c_1 + c_2 = 0 \Rightarrow c_2 = -c_1$$

- Substitution into the test wave-function shown in slide 8 leads to

$$\varphi(x) = c_1\left[x^2(L-x) - x(L-x)^2\right]$$

where c_1 can be determined from **normalization**. Thus

$$\boxed{\varphi(x) = -\sqrt{\frac{210}{L^7}}\left[x^2(L-x) - x(L-x)^2\right]}$$

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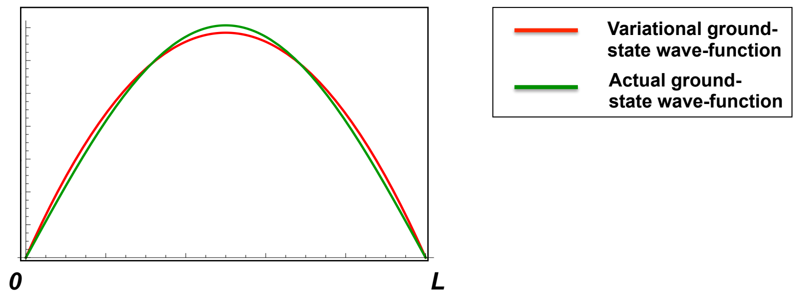
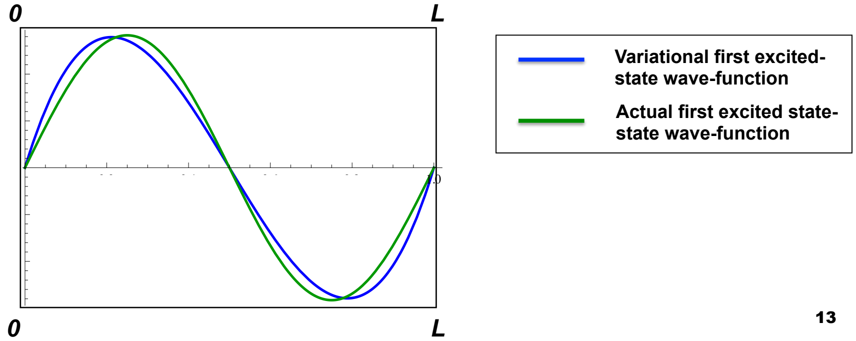
Graphic comparison of actual and variation wave-functions for a particle in a box





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