Lecture 16

Variational Principle

Study Goal of This Lecture

- Variational principle
- Solving the ground state harmonic oscillator with variational principle

16.1 Approximated Methods

In many-electron atoms, two things must be dealt with:

- electron-electon repulsion: no exact solution, approximated methods are needed.
- Pauli exclusion principle: considering of spin eigenstate and statistics.

and the approximated methods in quantum mechanics are:

- Variation principle
- Perturbation theory

Exact treatments end here at Hydrogen-like atoms. For more complex systems, no analytical exact solution exist. (Few other additional exactly solvable systems are particle in a spherical box, δ-function potential, finite-depth well and Morse potentail). In quantum mechanics, most useful approximated method are the variational principle and the perturbation theory, which have different applications. In this lecture, we briefly introduce the variational method, the perturbation thoery will be the optional materials. (However, perturbation theory is extremely useful in QM!) A more in-depth treatment of perturbation theory is out of the scope of this course since it is usually more mathematically involved. Nevertheless, the idea of "perturbation" is essential in physical chemistry, so we put it in the optional materials.

16.2 Variational theorem

The variational method is based on the following variational theorem:

Theorem 16.2.1. ***Variation theorem***

Given a system with a time-independent Hamiltonian $\hat{H}$. If ψ is a well-behaved wavefunction(trial wavefunction) of the system that satisfied the boundary conditions of the problem, then

$$\frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \geq E_0 \tag{16.1}$$

where E_0 is the ground state energy of $\hat{H}$,i.e. lowest eigenvalue of $\hat{H}$.

Since variational theorem usually involved many integrals, so it is most convenient to write down this theorem using Dirac's bracket notation:

$$|\psi\rangle \ \text{:trial wavefunction} \tag{16.2}$$

$$\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0. \tag{16.3}$$

The denominator is normalization condition. The variational theorem allows us to calculate an upper bound for the system's ground state energy.

Proof of variational theorem.

Assume the true orthornormal eigenbasis of $\hat{H}$ is $\{|\phi_n\rangle\}$:

$$\hat{H}\,|\phi_n\rangle = E_n\,|\phi_n\rangle\,, \tag{16.4}$$

then for an arbitrary $|\psi\rangle$, we can represent it as linear combination of $\{|\phi_n\rangle\}$(superposition principle)

$$|\psi\rangle = \sum_n C_n\,|\phi_n\rangle\,. \tag{16.5}$$

Therefore,

$$
\begin{aligned}
\langle\psi|\hat{H}|\psi\rangle &= \Big(\sum_n C_n^* \langle\phi_n|\Big)\hat{H}\Big(\sum_m C_m^* |\phi_m\rangle\Big) \\
&= \sum_{n,m} C_n^* C_m \langle\phi_n|\hat{H}|\phi_m\rangle \\
&= \sum_{n,m} C_n^* C_m E_m \langle\phi_n|\phi_m\rangle \\
&= \sum_{n,m} C_n^* C_m E_m \delta_{nm} \\
&= \sum_n |C_n|^2 E_n.
\end{aligned}
\tag{16.6}
$$

Similarly, $\langle\psi|\psi\rangle = \sum_n |C_n|^2$. Note that E_0 is the ground state, by definition

$$E_0 \leq E_1 \leq E_2 \leq \cdots \leq E_n \leq \cdots, \tag{16.7}$$

also, $|C_n|^2 \geq 0$, thus,

$$\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_n |C_n|^2 E_n}{\sum_n |C_n|^2} \geq \frac{\sum |C_n|^2 E_0}{\sum_n |C_n|^2} = E_0. \tag{16.8}$$

$\square$

Example given in the textbook, i.e. use a quadratic function to evaluate the ground state energy of a particle in a box, yields an upper bound. But, that is not a true variational treatment. We will consider a real example below:

16.3 Example: Harmonic Oscillator

Let's consider a harmonic oscillator, recall the Hamiltonian for harmonic oscillator:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \frac{-\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2. \tag{16.9}$$

To demonstrate the variational methods, we guess a trial function: a gaussion

$$\psi(x) = e^{-\alpha x^2}, \tag{16.10}$$

α is the variational parameter and it is greater than zero. (Otherwise it would not satisfy the boundary condition.)

We first calculate:

$$\int_{-\infty}^{\infty} \psi^* \psi dx = \int_{-\infty}^{\infty} e^{-\alpha x^2} e^{-\alpha x^2} dx = \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = \sqrt{\frac{\pi}{2\alpha}} \tag{16.11}$$

and

$$\begin{aligned}
\int_{-\infty}^{\infty} \psi^* \hat{H} \psi dx &= \int_{-\infty}^{\infty} e^{-\alpha x^2} \hat{H} e^{-\alpha x^2} dx \\
&= \int_{-\infty}^{\infty} e^{-\alpha x^2} \Big[\Big(\frac{-\hbar^2}{2m} \frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2} m\omega^2 x^2 \Big) e^{-\alpha x^2} \Big] dx \\
&= \int_{-\infty}^{\infty} e^{-\alpha x^2} \Big[\frac{-\hbar^2}{2m} \Big(-2\alpha e^{\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2} \Big) + \frac{1}{2} m\omega^2 x^2 e^{-\alpha x^2} \Big] dx \\
&= \int_{-\infty}^{\infty} \Big[\frac{\alpha \hbar^2}{m} e^{-2\alpha x^2} + \Big(\frac{1}{2} m\omega^2 - \frac{2\alpha^2 \hbar^2}{m} \Big) x^2 e^{-2a\alpha x^2} \Big] dx \\
&= \frac{\alpha \hbar^2}{m} \sqrt{\frac{\pi}{2\alpha}} + (\frac{1}{2} m\omega^2 - \frac{2\alpha^2\hbar^2}{m}) \frac{1}{8} \sqrt{\frac{2\pi}{\alpha^3}}.
\end{aligned} \tag{16.12}$$

Note that $\int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = \sqrt{\frac{2\pi}{4\alpha}}$ $\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{1}{8}\sqrt{\frac{2\pi}{\alpha^3}}$

So, now we define function f:

$$\begin{aligned}
f = \frac{\int \psi^* \hat{H} \psi dx}{\int \psi^* \psi dx} &= \frac{\frac{\alpha\hbar^2}{m}\sqrt{\frac{\pi}{2\alpha}} + (\frac{1}{2} m\omega^2 - \frac{2\alpha^2\hbar^2}{m}) \frac{1}{8} \sqrt{\frac{2\pi}{\alpha^3}}}{\sqrt{\frac{\pi}{2\alpha}}} \\
&= \frac{\alpha\hbar^2}{m} + \Big(\frac{1}{2} m\omega^2 - \frac{2\alpha^2\hbar^2}{m} \Big) \times \frac{1}{4\alpha} \\
&= \frac{\alpha\hbar^2}{2m} + \frac{m\omega^2}{8\alpha}.
\end{aligned} \tag{16.13}$$

In order to find the minimum of f, we differentiate it with respect to α

$$\frac{\mathrm{d}f}{\mathrm{d}\alpha} = 0 \Rightarrow \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0. \tag{16.14}$$

Finally, we obtain

$$\alpha^2 = \frac{m^2\omega^2}{4\hbar^2} \longrightarrow \alpha = \pm \frac{m\omega}{2\hbar}. \tag{16.15}$$

We find that the variational principle yield the exact ground state wavefunction for the harmonic oscillator. This is not surprising since the ground state, as we know, is an Gaussian.

A good choice of trial wavefunction form is essentail for the success of variational method. Normally, it requires many combinations of function to obtain optimal result.