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# Tutorial VII

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# Reminder

The variational method (Rayleigh-Ritz) is method for finding approximate solutions to the Schrödinger equation for a Hamiltonian $H$ and its corresponding eigenstates and energies. We are interested in finding eigenstates and eigenvalues of a time independent Hamiltonian defined by

$$H |\psi_n\rangle = E_n |\psi_n\rangle$$

Now assume we have a trial solution for the ground state $|\phi_0\rangle$, which in general can be decomposed in terms of a linear combination of eigenstates which serve as a complete orthonormal basis,

$$|\phi_0\rangle = \sum_n c_n |\psi_n\rangle$$

The energy of the trial solution is given by,

$$\begin{aligned} E(\phi_0) &= \frac{\langle\phi_0| H |\phi_0\rangle}{\langle\phi_0|\phi_0\rangle} \\ &= \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \end{aligned}$$

If we now consider the difference with respect to the energy of the ground state, we have,

$$E(\phi) - E_0 = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} - E_0 = \frac{\sum_n |c_n|^2 (E_n - E_0)}{\sum_n |c_n|^2}$$

and since $E_n \geq E_0$ for all $n$, we have $E(\phi) \geq E_0$.

The variational wavefunction will always yield an energy expectation value that is greater than or equal to the ground state energy. Equality is only satisfied if the approximate wavefunction is in fact the ground state wavefunction.

# EXERCISE I : Variational principle

The variational method (Rayleigh-Ritz) is method for finding approximate solutions to the Schrödinger equation for a Hamiltonian $H$ and its corresponding eigenstates and energies.

1. Write down a procedure for applying the variational method to approximate the ground state of an arbitrary time-independent Hamiltonian. How does the energy found via the variational method compare to the true ground state energy of the problem Hamiltonian ? How can you generalize the procedure to find excited states of the problem Hamiltonian ?

   **A procedure to find approximate ground state wavefunction and ground state energy** is thus,

   - Choose a functional form for trial wavefunction $|\phi(\alpha_1, \alpha_2, \cdots, \alpha_N)\rangle$ which depends on a set of parameters $\alpha_j$,
   - Calculate the energy expectation value $E\,|\phi(\alpha_j)\rangle = f(\alpha_j)$,
   - Minimize $f(\alpha_j)$, i.e.,

   $$\frac{\partial f(\alpha_j)}{\partial \alpha_1} = \frac{\partial f(\alpha_j)}{\partial \alpha_2} = \cdots = \frac{\partial f(\alpha_j)}{\partial \alpha_N} = 0$$

   The set of parameters and trial wavefunction that minimizes $f(\alpha_j)$ gives an approximation to $|\psi_0\rangle$ and the ground state energy $E_0$.

   **The variational principle can also be used to obtain excited states**,

   Suppose that we choose the trial function to the $i$th state, such that is it orthogonal to all lower energy states by imposing the condition $\langle \phi_i | \psi_{n'} \rangle = 0$ for $n' = 0, 1, 2, \cdots i - 1$.

   For example, to find the first excited state, we choose a trial function which is orthogonal to the ground state. Of course we don't always know the exact ground state wavefunction, but in many cases we can define an orthogonal trial state without knowing the ground state exactly. For example, by exploiting symmetry of the wavefunctions : assuming the Hamiltonian is symmetric with respect to some coordinate $x$, then the ground state will be a symmetric function of $x$. The first excited state will be an antisymmetric function. This can be generalized to more states, e.g. assuming states of a certain angular momentum $J$ to find a set of wavefunctions with different $J$ values.

2. Apply the variational method to find the ground state and the first excited state of the one-dimensional harmonic oscillator. Take as a trial function the exponential function $\Phi(a, x) = Ae^{-ax^2}$, where $A$ is a constant to be determined and $a$ is an adjustable parameter (taken to be a positive number).

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

in the $x$ representation, $p = -i\hbar\partial_x$,

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2$$

We can impose the normalization of the wavefunction, i.e., $\langle\phi|\phi\rangle = 1$,

$$1 = |A|^2 \int e^{-2ax^2}\mathrm{d}x$$

Meaning,

$$A = \left(\frac{2a}{\pi}\right)^{1/4}$$

$$\begin{aligned}
E(\phi) &= \langle\phi|\, H \,|\phi\rangle \\
&= |A|^2 \int e^{-ax^2}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right] e^{-ax^2}\mathrm{d}x \\
&= |A|^2 \int e^{-ax^2}\left[-\frac{\hbar^2}{2m}(-2a)(1-2ax^2)e^{-ax^2} + \frac{1}{2}m\omega^2 x^2 e^{-ax^2}\right]\mathrm{d}x \\
&= \sqrt{\frac{2a}{\pi}}\left(\frac{\sqrt{2\pi a}\hbar^2}{4m} + \frac{\sqrt{2\pi}m\omega^2}{16a^{3/2}}\right) \\
&= \frac{\hbar^2 a}{2m} + \frac{m\omega^2}{8a}
\end{aligned}$$

We search to minimize the energy,

$$\frac{\mathrm{d}E(\phi_0)}{\mathrm{d}a} = 0$$

And we find,

$$a = \frac{m\omega}{2\hbar}$$

And so,

$$E(\phi) = \frac{\hbar\omega}{2}$$

**Remark :** From the known solution,

$$\begin{cases} \psi_n(x) = \dfrac{1}{\sqrt{2^n n!}}\left(\dfrac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} H_n\left(\sqrt{\dfrac{m\omega}{\hbar}}x\right) \\ E_n = \hbar\omega\left(n + \dfrac{1}{2}\right) \end{cases}$$

It is indeed right.
For the first excited state now, we will need to have the orthonormalisation, meaning that $\langle 0|1\rangle = 0$, so we can choose $|1\rangle$ as being an odd function because $|0\rangle$ is an even one. Meaning,

$$\phi_1 = xAe^{-ax^2} \implies A = \left(\frac{32a^3}{\pi}\right)^{1/4}$$

$$\frac{\partial^2}{\partial x^2} xe^{-ax^2} = 2axe^{-ax^2}\left(2ax^2 - 3\right)$$

So,

$$\begin{aligned}
E(\phi_1) = \langle\phi_1|\, H\, |\phi_1\rangle &= A^2 \int_{-\infty}^{+\infty} xe^{-ax^2}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2\right] xe^{-ax^2}\mathrm{d}x \\
&= A^2 \int_{-\infty}^{+\infty} xe^{-ax^2}\left[-\frac{\hbar^2}{2m}2ax(2ax^2-3)e^{-ax^2} + \frac{1}{2}m\omega^2 x^3 e^{-ax^2}\right]\mathrm{d}x \\
&= A^2\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\left(-4a^2x^4e^{-2ax^2} + 6ax^2e^{-2ax^2}\right)\mathrm{d}x + A^2\frac{m\omega^2}{2}\int_{-\infty}^{+\infty} x^4 e^{-2ax^2}\mathrm{d}x \\
&= \left(\sqrt{\frac{32a^3}{\pi}}\right)\frac{\hbar^2}{2m}\left(-\frac{3}{8}\sqrt{\frac{2\pi}{a}} + \frac{3}{4}\sqrt{\frac{2\pi}{a}}\right) + \left(\sqrt{\frac{32a^3}{\pi}}\right)\frac{m\omega^2}{2}\frac{3}{32}\sqrt{\frac{2\pi}{a^5}} \\
&= \frac{3\hbar^2 a}{2m} + \frac{3m\omega^2}{8a}
\end{aligned}$$

$$\frac{\mathrm{d}E(\phi_1)}{\mathrm{d}a} = 0$$

And we find,

$$a = \frac{m\omega}{2\hbar}$$

And so,

$$E(\phi_1) = \frac{3\hbar\omega}{2}$$

Which is again the known solution.

3. We now choose as a trial function $\Phi(a,x) = A/(1+ax^2)$ where again $A$ is a constant to be determined. Calculate, by the variational method, the energy of the ground state of the harmonic oscillator. Compare your results with the previous question.

$$A = \left(\frac{2\sqrt{a}}{\pi}\right)^{1/2}$$

$$\begin{aligned}
E(\phi_0) &= \langle\phi_0|\, H \,|\phi_0\rangle \\
&= A^2 \int_{-\infty}^{+\infty} \frac{1}{1+ax^2}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2\right]\frac{1}{1+ax^2}\mathrm{d}x \\
&= A^2\left(\frac{\pi\hbar^2\sqrt{a}}{8m} + \frac{\pi m\omega^2}{4a^{3/2}}\right) \\
&= \frac{a\hbar^2}{4m} + \frac{m\omega^2}{2a}
\end{aligned}$$

And so,

$$\frac{\mathrm{d}E}{\mathrm{d}a}$$

We get,

$$a = \frac{\sqrt{2}m\omega}{\hbar}$$

And so we get,

$$E(\phi_0) = \frac{\hbar\omega}{2}$$

About 40% error with the true solution.