# Variational Method in quantum mechanics

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## 1 Theory

We attempt to guess the ground state energy $E_0$ by considering a "trial ket", $|\psi_0\rangle$, which tries to imitate the true ground-state ket $|\varphi_0\rangle$. We define

$$\overline{H} = \frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \tag{1}$$

((**Thoerem**))

$$\overline{H} = \frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \geq E_0$$

We can obtain an upper bound to $E_0$ by considering various kinds of $|\psi_0\rangle$.

((**Proof**))

$$|\psi_0\rangle = \sum_n |\varphi_n\rangle\langle\varphi_n|\psi_0\rangle$$

where $|\varphi_n\rangle$ is an exact energy eigenstate of $\hat{H}$

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$$

$$\begin{aligned}\overline{H} &= \frac{\langle\psi_0|\hat{H}\sum_n|\varphi_n\rangle\langle\varphi_n|\psi_0\rangle}{\sum_n|\langle\varphi_n|\psi_0\rangle|^2} = \frac{\sum_n E_n|\langle\varphi_n|\psi_0\rangle|^2}{\sum_n|\langle\varphi_n|\psi_0\rangle|^2} \\ &= E_0 + \frac{\sum_n (E_n - E_0)|\langle\varphi_n|\psi_0\rangle|^2}{\sum_n|\langle\varphi_n|\psi_0\rangle|^2} \geq E_0\end{aligned}$$

where $E_0$ is the exact ground-state energy.

$$\hat{H}|\varphi_0\rangle = E_0|\varphi_0\rangle$$

The equality sign in Eq.(1) holds only if $|\psi_0\rangle$ coincides exactly with $|\varphi_0\rangle$.

Another method to state the theorem is to assert that $\overline{H}$ is stationary with respect to the variation

$$|\psi_0\rangle = |\psi_0(\lambda_1, \lambda_2, \lambda_3, ..., \lambda_n)\rangle$$

with $\lambda_1$, $\lambda_2$, $\lambda_3$, ..., $\lambda_n$ are parameters.

$$\frac{\partial \overline{H}}{\partial \lambda_1} = 0, \frac{\partial \overline{H}}{\partial \lambda_2} = 0, \frac{\partial \overline{H}}{\partial \lambda_3} = 0, ...., \frac{\partial \overline{H}}{\partial \lambda_n} = 0 .$$

## 2 Example-1

Wave function for the ground state of the hydrogen

$$\psi_0(r) = e^{-r/a}$$

where $a$ is a parameter.

$$H = \frac{1}{2m}\boldsymbol{p}^2 - \frac{e^2}{r} = \frac{1}{2m}(p_r{}^2 + \frac{\boldsymbol{L}^2}{r^2}) - \frac{e^2}{r}$$

with

$$p_r = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r} r ,$$

Since $\boldsymbol{L}^2\psi_0 = 0$, we have

$$\begin{aligned}
H\psi_0 &= [\frac{1}{2m}(p_r{}^2 + \frac{\boldsymbol{L}^2}{r^2}) - \frac{e^2}{r}]\psi_0 \\
&= [\frac{1}{2m}p_r{}^2 - \frac{e^2}{r}]\psi_0 \\
&= \frac{-\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi_0) - \frac{e^2}{r}\psi_0 \\
&= \frac{-\hbar^2}{2m}[\psi_0'' + \frac{2}{r}\psi_0'] - \frac{e^2}{r}\psi_0 \\
&= \frac{-\hbar^2}{2m}(\frac{1}{a^2} - \frac{2}{ar})\psi_0 - \frac{e^2}{r}\psi_0
\end{aligned}$$

$$\overline{H} = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$\begin{aligned}
\langle \psi_0 | \hat{H} | \psi_0 \rangle &= \int \psi_0^*(\mathbf{r}) H \psi_0(\mathbf{r}) d\mathbf{r} \\
&= \int_0^\infty \left(\frac{-\hbar^2}{2ma^2} + \frac{\hbar^2}{mar} - \frac{e^2}{r}\right) e^{-2r/a} (4\pi r^2 dr) \\
&= 4\pi \int_0^\infty \left(\frac{-\hbar^2}{2ma^2} r^2 + \frac{\hbar^2}{ma} r - e^2 r\right) e^{-2r/a} dr) \\
&= 4\pi \frac{a(-2ae^2 m + \hbar^2)}{8m}
\end{aligned}$$

$$\langle \psi_0 | \psi_0 \rangle = \int |\psi_0(\mathbf{r})|^2 d\mathbf{r} = \int_0^\infty e^{-2r/a} 4\pi r^2 dr = 4\pi \frac{a^3}{4}$$

Note that

$$\int_0^\infty e^{-\alpha r} r^n dr = \frac{n!}{\alpha^{n+1}}.$$

Then we have

$$\overline{H} = \frac{\hbar^2}{2ma^2} - \frac{e^2}{a}$$

$$\frac{\partial \overline{H}}{\partial a} = \frac{\hbar^2}{2m}\left(-\frac{2a}{a^4}\right) + \frac{e^2}{a^2} = 0$$

or

$$a_0 = \frac{\hbar^2}{me^2}. \qquad \text{(Bohr radius)}$$

Therefore

$$\tilde{\psi}_0(r) = e^{-r/a_0}$$

$$\overline{H} = -\frac{e^2}{2a_0},$$

which is correct ground state energy.

## 3 Example-2: Simple harmonics

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2 x^2$$

We assume that

$$\psi_0(x) = e^{-\alpha x^2}$$

where $\alpha$>0 (even function).

$$\overline{H} = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$\langle \psi_0 | \psi_0 \rangle = \int |\psi_0(x)|^2 dx = \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = \sqrt{\frac{\pi}{2\alpha}}$$

$$\begin{aligned}
\langle \psi_0 | \hat{H} | \psi_0 \rangle &= \int \psi_0{}^*(x) H \psi_0(x) dx \\
&= \int_{-\infty}^{\infty} e^{-\alpha x^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2 x^2\right) e^{-\alpha x^2} dx \\
&= \int_{-\infty}^{\infty} e^{-2\alpha x^2} \frac{1}{2m}[m^2 x^2 \omega^2 + 2\alpha\hbar^2(1-2\alpha x^2)] dx \\
&= \sqrt{\frac{\pi}{2}} \frac{(m^2\omega^2 + 4\alpha^2\hbar^2)}{8m\alpha^{3/2}}
\end{aligned}$$

Then we have

$$\overline{H} = \frac{m^2\omega^2 + 4\alpha^2\hbar^2}{8m\alpha}$$

$$\frac{\partial \overline{H}}{\partial \alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0$$

or

$$\alpha = \alpha_0 = \frac{m\omega}{2\hbar}$$

$$\tilde{\psi}_0(x) = e^{-\frac{m\omega}{2\hbar}x^2}$$

$$\overline{H}(\alpha_0) = \frac{1}{2}\hbar\omega_0$$

## 4 Example-III Sakurai

The ground state of one-dimensional harmonics

Trial function

$$\langle x|\tilde{0}\rangle = e^{-\beta|x|} \qquad (\beta>0).$$

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2$$

$$\langle\tilde{0}|\tilde{0}\rangle = 2\int_0^\infty e^{-2\beta x}dx = \frac{1}{\beta}$$

$$\overline{H} = \frac{\langle\tilde{0}|\hat{H}|\tilde{0}\rangle}{\langle\tilde{0}|\tilde{0}\rangle}$$

$$I = \langle\tilde{0}|\hat{H}|\tilde{0}\rangle = \int_{-\infty}^{\infty} e^{-\beta|x|}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{-\beta|x|}dx$$

or

$$\begin{aligned} I &= \int_{-\infty}^{-\varepsilon} e^{\beta x}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{\beta x}dx \\ &+ \int_{\varepsilon}^{\infty} e^{-\beta x}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{-\beta x}dx + \int_{-\varepsilon}^{\varepsilon} e^{-\beta|x|}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{-\beta|x|}dx \end{aligned}$$

In the first term of *I*, we put *x*' = -*x*

$$\int_{\infty}^{\varepsilon}(-\frac{\hbar^2}{2m}\beta^2 + \frac{1}{2}m\omega_0{}^2x'^2)e^{-2\beta x'}(-1)dx' = \int_{\varepsilon}^{\infty}(-\frac{\hbar^2}{2m}\beta^2 + \frac{1}{2}m\omega_0{}^2x^2)e^{-2\beta x}dx$$

Then

$$I = 2\int_{\varepsilon}^{\infty} \left(-\frac{\hbar^2}{2m}\beta^2 + \frac{1}{2}m\omega_0{}^2x^2\right)e^{-2\beta x}dx + \int_{-\varepsilon}^{\varepsilon} e^{-\beta|x|}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2\right)e^{-\beta|x|}dx$$

in the limit of $\varepsilon \to 0$.

Noting that

$$\int_0^{\infty} x^2 e^{-ax} = \frac{2}{a^3}$$

$I$ is calculated as

$$I = -\frac{\hbar^2}{2m}\beta + \frac{m\omega_0{}^2}{4\beta^3} + \int_{-\varepsilon}^{\varepsilon} e^{-\beta|x|}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2\right)e^{-\beta|x|}dx$$

We now consider the second term

$$f(x) = e^{-\beta|x|}$$

This function $f(x)$ is continuous at $x = 0$, but d$f$/d$x$ is discontinuous at $x = 0$.

d$f$/d$x$=-$\beta$ exp(-$\beta x$) for $x$>0 and $\beta$ exp($\beta x$) for $x$<0.

$$I_2 = \int_{-\varepsilon}^{\varepsilon} e^{-\beta|x|}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2\right)e^{-\beta|x|}dx = -\frac{\hbar^2}{2m}\int_{-\varepsilon}^{\varepsilon} f(x)\frac{d^2 f(x)}{dx^2}dx$$

Note that (d$f$/d$x$)$^2$ is continuous at $x = 0$.

$$\int_{-\varepsilon}^{\varepsilon} f(x)\frac{d^2 f(x)}{dx^2}dx = [f(x)\frac{df(x)}{dx}]_{-e}^{\varepsilon} - \int_{-\varepsilon}^{\varepsilon}[\frac{df(x)}{dx}]^2 dx = f(0)[\frac{df(x)}{dx}|_{x=\varepsilon} - \frac{df(x)}{dx}|_{x=-\varepsilon}] = -2\beta$$

Then we have

$$I_2 = \frac{\hbar^2\beta}{m}$$

or

$$I = -\frac{\hbar^2}{2m}\beta + \frac{m\omega_0{}^2}{4\beta^3} + \frac{\hbar^2\beta}{m} = \frac{\hbar^2}{2m}\beta + \frac{m\omega_0{}^2}{4\beta^3}$$

$$\overline{H} = \frac{I}{(1/\beta)} = \beta\left(\frac{\hbar^2}{2m}\beta + \frac{m\omega_0^{\ 2}}{4\beta^3}\right) = \frac{\hbar^2}{2m}\beta^2 + \frac{m\omega_0^{\ 2}}{4\beta^2} \geq 2\sqrt{\frac{\hbar^2}{2m}\beta^2 \frac{m\omega_0^{\ 2}}{4\beta^2}} = \frac{1}{\sqrt{2}}\hbar\omega_0$$

The equality is valid when

$$\beta^4 = \frac{m^2\omega_0^{\ 2}}{2\hbar^2}$$

## 5. Mathematica-I

```
Clear["Global`*"]; ψ[x_] := A Exp[-α x^2];
H1 := (-ℏ^2/(2 m) D[#, {x, 2}] + 1/2 m ω^2 x^2 #) &;
```

```
f1 = ψ[x] H1[ψ[x]] // Simplify
```

$$\frac{A^2 e^{-2 x^2 \alpha} \left(m^2 x^2 \omega^2 + 2 \alpha \left(1 - 2 x^2 \alpha\right) \hbar^2\right)}{2 m}$$

```
K1 = Integrate[f1, {x, -∞, ∞}] // Simplify[#, α > 0] &
```

$$\frac{A^2 \sqrt{\frac{\pi}{2}} \left(m^2 \omega^2 + 4 \alpha^2 \hbar^2\right)}{8 m \alpha^{3/2}}$$

```
f2 = ψ[x] ψ[x] // Simplify
```

$$A^2 e^{-2 x^2 \alpha}$$

```
K2 = Integrate[f2, {x, -∞, ∞}] // Simplify[#, α > 0] &
```

$$\frac{A^2 \sqrt{\frac{\pi}{2}}}{\sqrt{\alpha}}$$

```
K12 = K1 / K2 // Simplify
```

$$\frac{m\,\omega^2}{8\,\alpha} + \frac{\alpha\,\hbar^2}{2\,m}$$

```
eq1 = Solve[D[K12, α] == 0, α]
```

$$\left\{\left\{\alpha \to -\frac{m\,\omega}{2\,\hbar}\right\}, \left\{\alpha \to \frac{m\,\omega}{2\,\hbar}\right\}\right\}$$

```
E0 = K12 /. eq1[[2]] // Simplify
```

$$\frac{\omega\,\hbar}{2}$$

## 6. Mathematica-II

```
Clear["Global`*"];
H1 := (-ℏ^2/(2 m) 1/r D[r #, {r, 2}] - e1^2/r #) &;
ψ[r_] := A Exp[-α r^2];
```

```
f1 = Integrate[ψ[r] H1[ψ[r]] 4 π r^2, {r, 0, ∞}] //
  Simplify[#, α > 0] &
```

$$-\frac{A^2 \pi \left(8\, e1^2\, m - 3 \sqrt{2 \pi} \sqrt{\alpha}\, \hbar^2\right)}{8\, m\, \alpha}$$

```
f2 = Integrate[ψ[r] ψ[r] 4 π r^2, {r, 0, ∞}] //
  Simplify[#, α > 0] &
```

$$\frac{A^2 \pi^{3/2}}{2 \sqrt{2}\, \alpha^{3/2}}$$

```
K = f1 / f2 // Simplify
```

$$-2\, e1^2 \sqrt{\frac{2}{\pi}} \sqrt{\alpha} + \frac{3\, \alpha\, \hbar^2}{2\, m}$$

```
eq1 = Solve[D[K, α] == 0, α]
```

$$\left\{\left\{\alpha \to \frac{8\, e1^4\, m^2}{9\, \pi\, \hbar^4}\right\}\right\}$$

```
E0 = K /. eq1[[1]] //
  FullSimplify[#, {e1 > 0, m > 0, ℏ > 0}] &
```

$$-\frac{4\, e1^4\, m}{3\, \pi\, \hbar^2}$$

## 7. Example (J.L. Martin, Basic Quantum Mechanics, p.199)

We consider the 1D quantum box. A particle is confined in one dimension to the range $0 \le x \le 1$. The requirements on the energy eigenfunction $\psi(x)$ are

$$-\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

with the boundary condition

$$\psi(x=0) = \psi(x=1) = 0 .$$

For simplicity we drop all the physical constants. We know the solution of the ground state,

$$E_0 = \pi^2 = 9.8696, \qquad \psi(x) = \sin(\pi x)$$

We now solve this problem by using a trial function (un-normalized) such that

$$\psi(x) = x^\alpha (1-x)^\alpha$$

We calculate

$$E_{trial}(\alpha) = \frac{-\int_0^1 \psi^*(x)\frac{d^2}{dx^2}\psi(x)dx}{\int_0^1 \psi^*(x)\psi(x)dx},$$

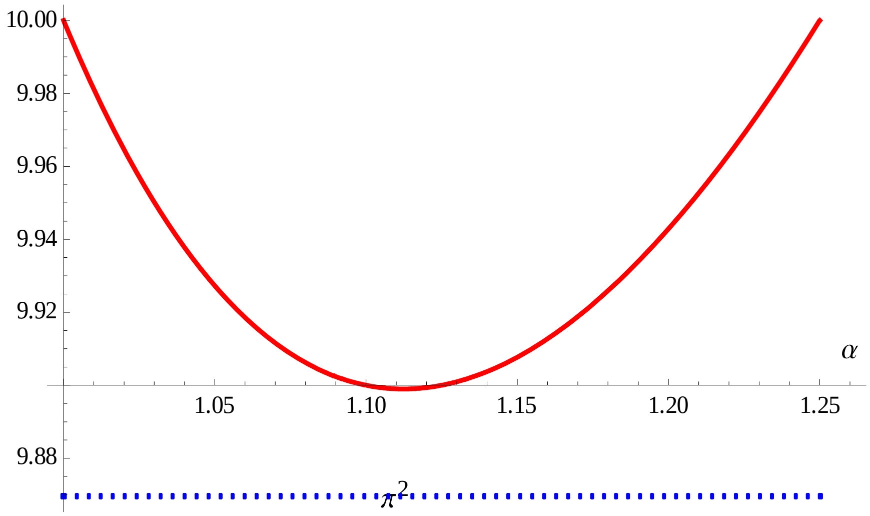
by using Mathematica. After that we vary the parameter $\alpha$ to obtain the minimum value of $E_{trial}(\alpha)$. We find the minimum value of $E_{trial}(\alpha)$ (= 9.89898) at $\alpha = 1.11237$. This value is a littler larger than the actual ground state energy: $E_0 = \pi^2 = 9.8696$

((**Mathematica**))

```
Clear["Global`*"]; ψ1 = x^α (1 - x)^α; f1 = ψ1 D[ψ1, {x, 2}] ;
f2 = ψ1^2 ;
```

$$E1 = \frac{-\int_0^1 f1\, dx}{\int_0^1 f2\, dx} \text{ // Simplify[\#, } \alpha > 1/2\text{] \&;}$$

```
h1 = Plot[E1, {α, 1.0, 1.25}, PlotStyle → {Red, Thick},
  PlotRange → All];
h2 =
 Graphics[{Text[Style["α", Black, 12], {1.26, 9.91}],
   Text[Style["π^2", Black, 12], {1.11, π^2}],
   Blue, Dotted, Thick, Line[{{1, π^2}, {1.25, π^2}}]}];
Show[h1, h2]
```




```
FindMinimum[E1, {α, 1.1}]
```

{9.89898, {α → 1.11237}}

```
π^2 // N
```

9.8696