Variational Method in quantum mechanics

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We consider the variational method and apply it to just one type of problem, the estimation of the ground state energy eigenvalue of a quantum system.

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

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

((**Theorem**))

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

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 $\hat{H}$

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

Then we have

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

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 λ_1, λ_2, λ_3, ..., λ_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 (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

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

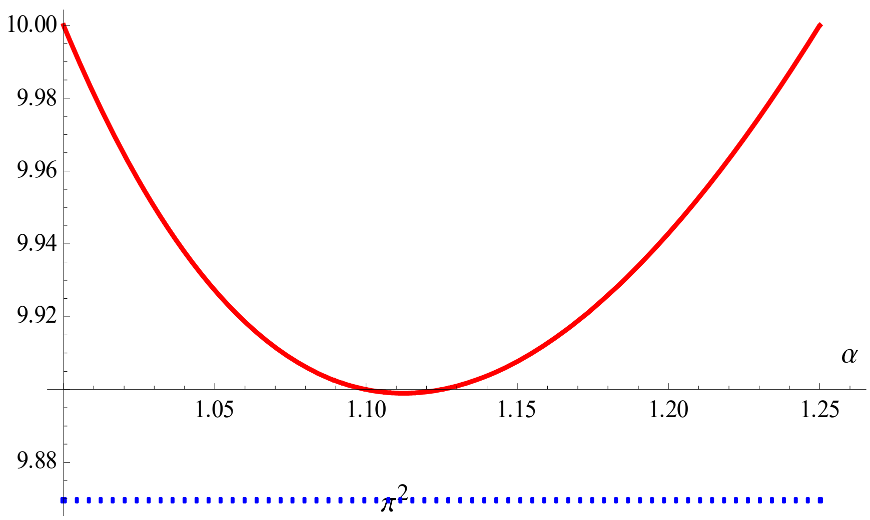
by using Mathematica. After that we vary the parameter α to obtain the minimum value of $E_{trial}(\alpha)$. We find the minimum value of $E_{trial}(\alpha)$ (= 9.89898) at $\alpha = 1.11237$. This value is a littler larger than the actual ground state energy: $E_0 = \pi^2 = 9.8696$

((**Mathematica**))

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

E1 = (-∫_0^1 f1 ⅆx)/(∫_0^1 f2 ⅆx) // Simplify[#, α > 1/2] &;

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

3 Example: ground state of hydrogen

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

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

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

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

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

Note that

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

Then we have

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

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

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.

4. Example

Wave function for the ground state of the hydrogen

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

where α is a parameter. We use the method which is used above. Using Mathematica, we get the following results;

$$\alpha = \frac{8e^4 m^2}{9\pi\hbar^4} = \frac{8}{9\pi {a_B}^2} = \frac{0.282942}{{a_B}^2} = \left(\frac{0.531}{a_B}\right)^2$$

and the upper limit of the ground state energy as

$$E = -\frac{4e^4 m}{3\pi\hbar^2} = -\frac{8}{3\pi} R = -0.848826R > -R$$

where

$$a_B = \frac{e^2}{m\hbar^2}, \qquad R = \frac{me^4}{2\hbar^2}, \qquad E_{n=1} = -R = -\frac{me^4}{2\hbar^2}.$$

((**Mathematica**))

```
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}] &
```

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

5 Example: 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 α>0 (even function).

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

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

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

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

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

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

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

6. Example from Sakurai

The ground state of one-dimensional harmonics

Trial function

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

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

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

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

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

or

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

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

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

Then

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

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

Noting that

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

I is calculated as

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

We now consider the second term

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

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

df/dx=-β exp(-βx) for x>0 and β exp(βx) for x<0.

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

Note that (df/dx)^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

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

7. Mathematica

```
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
```

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

REFERENCES

J.J. Sakurai and J. Napolitano, *Modern Quantum Mechanics*, 2nd edition (Addison-Wesley, 2011).

J.L. Martin, Basic Quantum Mechanics (Oxford, 1981).