Chapter 13

The Variational Method

The variational method is an approximation procedure that we will use to establish an upper bound for a ground state energy. Approximation methods, including the variational method, the WKB method (chapter 14), time-independent (chapter 15) and time-dependent (chapter 16) perturbation theory, are important because there are relatively few quantum mechanical problems of interest which can be solved exactly.

> Variational methods are widely applied in classical and quantum mechanics. They are closely related to the calculus of variations. The discovery of variational methods has origins with the ancient Greeks, notably Aristotle, and has been applied by Fermat, Maupertius, Euler, Lagrange, Hamilton, and others.[1] The procedure discussed here was originally used by Lord Rayleigh in 1873 to compute vibration frequencies of mechanical systems.[2] The path integral of Feynman is intrisically linked to variational principles. The Hartree-Fock method of calculating approximate wave functions is a variational method.
>
> Among important applications are many body problems which no one knows how to solve exactly. Multi-electron atoms and molecules are many body systems. The theory of superconductivity is based on variational methods.

Here is a roadmap to establish an upper bound on a ground state energy.

step 1) Guess a good trial wave function $|\psi>$,
step 2) calculate
$$\frac{<\psi|\mathcal{H}|\psi>}{<\psi|\psi>},$$
and this is an upper bound on the ground state energy, *i.e.*,
$$E_0 \leq \frac{<\psi|\mathcal{H}|\psi>}{<\psi|\psi>},$$
step 3) adjust your guess of the wave function $|\psi>$ to reduce the upper bound for the ground state energy E_0.

The key here is the first step. If you guess poorly, you will attain a large upper bound that may not be satisfying or helpful. If you guess well, the upper bound may be useful. If you guess perfectly, *i.e.*, if you guess the actual wave function, you saturate the inequality and attain the ground state energy.

Why does this work? For any $|\psi>$, we can expand in any eigenbasis, including the energy eigenbasis, so
$$|\psi> = \mathcal{I}|\psi> = \sum_i |E_i><E_i||\psi> .$$

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[1] Yourgrau and Mandelstam, *Variational Principles in Dynamics and Quantum Theory* (Dover Publications, Inc., New York, 1968), 3rd ed.

[2] Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1968), 3rd ed.

We will substitute this for the expression in step 2 above. To simplify the calculation, we assume the wave function is normalized, so $<\psi|\psi> = 1$. Then

$$\frac{<\psi|\mathcal{H}|\psi>}{<\psi|\psi>} = <\psi|\mathcal{H}|\psi>$$

$$= <\psi|\mathcal{I}|\mathcal{H}|\mathcal{I}|\psi>$$

$$= <\psi|\sum_i |E_i><E_i||\mathcal{H}|\sum_j |E_j><E_j||\psi>$$

$$= \sum_i \sum_j <\psi|E_i><E_i|\mathcal{H}|E_j><E_j|\psi> \tag{1}$$

$$= \sum_i \sum_j <\psi|E_i><E_i|E_j|E_j><E_j|\psi> \tag{2}$$

$$= \sum_i \sum_j <\psi|E_i> E_j <E_i|E_j><E_j|\psi> \tag{3}$$

$$= \sum_i \sum_j <\psi|E_i> E_j \delta_{ij} <E_j|\psi> \tag{4}$$

$$= \sum_i <\psi|E_i> E_i <E_i|\psi> \tag{5}$$

$$= \sum_i E_i \left| <E_i|\psi> \right|^2.$$

Since the ground state energy is the lowest energy in the system, $E_i \geq E_0$, for all E_i, so

$$\sum_i E_i \left| <E_i|\psi> \right|^2 \geq \sum_i E_0 \left| <E_i|\psi> \right|^2$$

$$= E_0 \sum_i \left| <E_i|\psi> \right|^2 \tag{6}$$

$$= E_0,$$

$$\Rightarrow \quad <\psi|\mathcal{H}|\psi> \geq E_0 \quad \text{for all } |\psi>.$$

A few comments are appropriate. In equation (1), we let the Hamiltonian operate to the right so is replaced by an eigenvalue in equation (2). The eigenvalue is constant so can be removed from the bracket per equation (3). The resulting bracket is a Kronecker delta, a form of $<i|j> = \delta_{ij}$, and is so denoted in equation (4). Since the Kronecker delta is zero if $i \neq j$, equation (5) is summed only over i because we get nonzero terms only when $i = j$. Finally, recognize $\sum \left| <E_i|\psi> \right|^2 = 1$ in equation (6), means $\sum \left| <E_i|\psi> \right|^2$ is a complete expansion over all states, so is 1 for a normalized wave function.

Also, the derivation assumes the system has bound states only. If the system has both bound and scattering states, such as a finite square well or finite harmonic oscillator, the summations must be replaced by $\sum\!\!\!\!\!\int$. This means you sum over bound states and integrate over scattering states. Other than replacing this symbol, the argument remains unchanged.

If you guess perfectly,

$$<\psi|\mathcal{H}|\psi> = <E_0|\mathcal{H}|E_0> = <E_0|E_0|E_0> = E_0 <E_0|E_0> = E_0,$$

i.e., you get the ground state energy. If you pick a trial wave function which is not perfect, you have $|\psi> = |E_0> + |\delta\psi>$,

$$
\begin{aligned}
\Rightarrow \quad <\psi|\mathcal{H}|\psi> &= (<E_0| + <\delta\psi|)\,|\mathcal{H}|\,(|E_0> + |\delta\psi>) \\
&= <E_0|\mathcal{H}|E_0> + <E_0|\mathcal{H}|\delta\psi> + <\delta\psi|\mathcal{H}|E_0> + <\delta\psi|\mathcal{H}|\delta\psi> \\
&= <E_0|E_0|E_0> + <E_0|E_0|\delta\psi> + <\delta\psi|E_0|E_0> + <\delta\psi|\mathcal{H}|\delta\psi> \quad (7)\\
&= E_0 <E_0|E_0> + E_0 <E_0|\delta\psi> + E_0 <\delta\psi|E_0> + <\delta\psi|\mathcal{H}|\delta\psi> \\
&= E_0 + 0 + 0 + <\delta\psi|\mathcal{H}|\delta\psi> \\
&= E_0 + \vartheta\left[(\delta\psi)^2\right],
\end{aligned}
$$

so the error is quadratic. Note in equation (7) the eigenvalue is present because the Hamiltonian operated to the left in the second term and to the right in the third term. The Hamiltonian can operate in either direction because it is Hermitian. Both the second and third terms are zero because $|E_0>$ and $|\delta\psi>$ must be orthogonal; $|\delta\psi>$ cannot contain any $|E_0>$ since $|E_0>$ has accounted for all of that component. Said another way, if $|\delta\psi>$ were to contain any $|E_0>$, it would be removed and added back into $|E_0>$.

The key is a good trial wave function. You can make a good guess at a good trial wave function by considering
1) is parity conserved? Is the wave function even or odd?
2) How does the wave function approach zero? Model the asymptotes correctly.
3) Pick something you can integrate. Numerical integration is appropriate if analytic integration is not. The integral must converge in any instance.

A Gaussian wave function is a popular trial wave function. The Gaussian integral is reviewed in Appendix A.

In practice, $\mathcal{H} = \mathcal{T} + \mathcal{V}$, so

$$
<\psi|\mathcal{H}|\psi> = <\psi|\mathcal{T} + \mathcal{V}|\psi> = <\psi|\mathcal{T}|\psi> + <\psi|\mathcal{V}|\psi> .
$$

These are evaluated as integrals. The differential kinetic energy operator is often convenient.

A few examples to illustrate the theory are in order.

A one dimensional infinite square well with walls at $-L$ and L, as was discussed in chapter 6, is a particularly simple example because we generally define $V = 0$ inside the well. Using a trial wave function of

$$
\psi(x) = \sqrt{\frac{1}{L}} \cos\left(\frac{\pi x}{2L}\right),
$$

we should get the exact ground state energy because we are using the exact ground state wave function as a trial wave function. We also know it is normalized. Here $\mathcal{H} = \mathcal{T} + \mathcal{V} = \mathcal{T}$ in the

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area of interest so

$$
\begin{aligned}
<\psi|\mathcal{H}|\psi> &= <\psi|\mathcal{T}|\psi> \\
&= \int_{-L}^{L} \sqrt{\frac{1}{L}} \cos^* \left(\frac{\pi x}{2L}\right) \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right) \sqrt{\frac{1}{L}} \cos\left(\frac{\pi x}{2L}\right) dx \\
&= -\frac{\hbar^2}{2mL} \int_{-L}^{L} \cos\left(\frac{\pi x}{2L}\right) \frac{d^2}{dx^2} \cos\left(\frac{\pi x}{2L}\right) dx \\
&= -\frac{\hbar^2}{2mL} \int_{-L}^{L} \cos\left(\frac{\pi x}{2L}\right) \frac{d}{dx}\left(-\sin\left(\frac{\pi x}{2L}\right)\frac{\pi}{2L}\right) dx \\
&= -\frac{\hbar^2}{2mL} \int_{-L}^{L} \cos\left(\frac{\pi x}{2L}\right) \left(-\cos\left(\frac{\pi x}{2L}\right)\frac{\pi^2}{4L^2}\right) dx \\
&= \frac{\hbar^2 \pi^2}{8mL^3} \int_{-L}^{L} \cos^2\left(\frac{\pi x}{2L}\right) dx.
\end{aligned}
$$

Using[3]

$$
\int \cos^2(ax)\, dx = \frac{1}{2}x + \frac{1}{4a}\sin(2ax),
$$

where $a = \pi/2L$ for our integral,

$$
\begin{aligned}
<\psi|\mathcal{H}|\psi> &= \frac{\hbar^2 \pi^2}{8mL^3} \left[\frac{1}{2}x + \frac{2L}{4\pi}\sin\left(\frac{\pi}{L}x\right)\right]_{-L}^{L} \\
&= \frac{\hbar^2 \pi^2}{8mL^3} \left[\frac{1}{2}L + \frac{2L}{4\pi}\sin(\pi) - \frac{1}{2}(-L) - \frac{2L}{4\pi}\sin(-\pi)\right] \\
&= \frac{\hbar^2 \pi^2}{8mL^3} \left[\frac{1}{2}L + 0 + \frac{1}{2}L - 0\right]
\end{aligned}
$$

$$
\boxed{\;\Rightarrow\quad <\psi|\mathcal{H}|\psi> = \frac{\hbar^2 \pi^2}{8mL^2},\;}
$$

which we know to be the exact ground state energy, as advertised.

A more practical example is

$$
V(x) = \alpha x^6 \qquad \text{using the Gaussian trial wave function} \qquad \psi(x) = Ae^{-bx^2}.
$$

Note when the potential is defined in position space, the potential energy function is not an operator. The potential has the general shape of a simple harmonic oscillator except with steeper walls. The constant b in the trial wave function is the parameter which will be varied. In choosing a Gaussian trial wave function, we will have a number of Gaussian integrals to evaluate.

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[3] form 302, page 313, *CRC Standard Math Tables* (CRC Press, Boca Raton, Florida, 1981), 26th ed.

Gaussian integrals are discussed in Appendix A. Normalizing the wave function simplifies the notation because we then do not have to explicitly carry a denominator, so

$$<\psi|\psi> = 1 = \int_{-\infty}^{\infty} \left(Ae^{-bx^2}\right)^* Ae^{-bx^2}\, dx = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\, dx = |A|^2 \sqrt{\frac{\pi}{2b}}$$

$$\Rightarrow \quad A = \left(\frac{2b}{\pi}\right)^{1/4} \quad \text{and} \quad A^2 = \sqrt{\frac{2b}{\pi}}.$$

Note this is independent of the potential, so we have determined the normalization constant for all potentials where we would use a Gaussian trial wave function.

We need the expectation value of the Hamiltonian, which we will calculate

$$<\psi|\mathcal{H}|\psi> = <\psi|\mathcal{T}|\psi> + <\psi|\mathcal{V}|\psi>,$$

where again, the first term is independent of the potential so is dependent only on the trial wave function. The expectation value of kinetic energy for a Gaussian trial wave function is calculated

$$<\psi|\mathcal{T}|\psi> = \int_{-\infty}^{\infty} \left(Ae^{-bx^2}\right)^* \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right) Ae^{-bx^2}\, dx = -|A|^2 \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2} e^{-bx^2}\, dx$$

We need the second derivative of the Gaussian exponential so

$$\frac{d}{dx} e^{-bx^2} = -2bx e^{-bx^2}$$

$$\Rightarrow \quad \frac{d^2}{dx^2} e^{-bx^2} = \frac{d}{dx}\left(-2bx e^{-bx^2}\right) = -2b\left(e^{-bx^2} + x(-2bx)e^{-bx^2}\right) = -2be^{-bx^2} + 4b^2x^2 e^{-bx^2}$$

$$\Rightarrow \quad <\psi|\mathcal{T}|\psi> = -|A|^2 \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} e^{-bx^2} \left(-2be^{-bx^2} + 4b^2x^2 e^{-bx^2}\right)\, dx$$

$$= -|A|^2 \frac{\hbar^2}{2m}\left[-2b \int_{-\infty}^{\infty} e^{-2bx^2}\, dx + 4b^2 \int_{-\infty}^{\infty} x^2 e^{-2bx^2}\, dx\right]$$

$$= -|A|^2 \frac{\hbar^2}{2m}\left[-2b \int_{-\infty}^{\infty} e^{-2bx^2}\, dx + 8b^2 \int_{0}^{\infty} x^2 e^{-2bx^2}\, dx\right]$$

where have used the fact all terms of the second integrand are even functions of x, and is an integral with symmetric limits so we can double the value of the integral from zero to the upper limit and get the same result. The first integral is Gaussian, and is evaluated in Appendix A. The second we evaluate the integral using[4]

$$\int_{0}^{\infty} x^{2n} e^{-px^2}\, dx = \frac{(2n-1)\cdots 5\cdot 3\cdot 1}{2(2p)^n}\sqrt{\frac{\pi}{p}} \quad \text{for} \quad p > 0, \quad \text{and} \quad n = 0, 1, 2, 3, \ldots,$$

[4] Form 15.3.1.26, page 249, *Handbook of Mathematical Formulas and Integrals* by Jeffrey

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where $n = 1$ and $p = 2b$ for our integral. Then

$$<\psi|T|\psi> = -\sqrt{\frac{2b}{\pi}}\frac{\hbar^2}{2m}\left[-2b\sqrt{\frac{\pi}{2b}} + 8b^2\frac{1}{2(2\cdot 2b)}\sqrt{\frac{\pi}{2b}}\right]$$

$$= \frac{\hbar^2}{2m}\left[2b\sqrt{\frac{2b}{\pi}}\sqrt{\frac{\pi}{2b}} - b\sqrt{\frac{2b}{\pi}}\sqrt{\frac{\pi}{2b}}\right] = \frac{\hbar^2}{2m}[2b - b]$$

$$\boxed{\Rightarrow \quad <\psi|T|\psi> = \frac{\hbar^2 b}{2m}.}$$

The expectation value of the potential energy for $V(x) = \alpha x^6$ is

$$<\psi|V|\psi> = \int_{-\infty}^{\infty}\left(Ae^{-bx^2}\right)^*\left(\alpha x^6\right)Ae^{-bx^2}\,dx = \alpha A^2\int_{-\infty}^{\infty}x^6 e^{-2bx^2}\,dx = 2\alpha A^2\int_0^{\infty}x^6 e^{-2bx^2}\,dx$$

where again, all terms of the integrand are even functions of x, and the integral has symmetric limits so we can double the value of the integral from zero to the upper limit and get the same result. Using the same form from Jeffrey, where $n = 3$ and $p = 2b$, the integral is

$$\boxed{<\psi|V|\psi> = 2\alpha A^2\int_0^{\infty}x^6 e^{-2bx^2}\,dx = 2\alpha\sqrt{\frac{2b}{\pi}}\frac{5\cdot 3\cdot 1}{2(2\cdot 2b)^3}\sqrt{\frac{\pi}{2b}} = \frac{15\alpha}{64b^3}.}$$

Adding these gives us what we started out to attain, or

$$\boxed{<\psi|\mathcal{H}|\psi> = <\psi|T|\psi> + <\psi|V|\psi> = \frac{\hbar^2 b}{2m} + \frac{15\alpha}{64b^3}}$$

We use a technique from introductory calculus to vary the parameter b. E_0 will be the minimum energy of any eigenstate in the system. If we take a derivative with respect to b, set that derivative equal to zero, and solve for the value of b which makes the statement true, we will find the value of $b = b_0$ which provides the lowest upper bound for this trial wave function. So

$$\frac{d}{db}\left(\frac{\hbar^2}{2m}b + \frac{15\alpha}{64}b^{-3}\right) = \frac{\hbar^2}{2m} - 3\frac{15\alpha}{64}\frac{1}{b^4} = 0$$

$$\Rightarrow \quad b_0^4 = \frac{45\alpha}{64}\frac{2m}{\hbar^2} = \frac{45\alpha}{32}\frac{m}{\hbar^2}$$

$$\boxed{\Rightarrow \quad b_0 = \left(\frac{3^2\cdot 5\cdot\alpha m}{2^5\hbar^2}\right)^{1/4}.}$$

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We have expressed this using powers of prime numbers as a technique to simplify the reduction. Using this value of the varied parameter yields the minimum energy for a Gaussian trial wave function. All that is left to do is the addition

$$<\psi|\mathcal{H}|\psi>_{\min} = <\psi|\mathcal{T}|\psi>\Big|_{b_0} + <\psi|V|\psi>\Big|_{b_0} = \frac{\hbar^2 b_0}{2m} + \frac{15\alpha}{64 b_0^3}$$

$$= \frac{\hbar^2}{2m}\left(\frac{3^2 \cdot 5 \cdot \alpha m}{2^5 \hbar^2}\right)^{1/4} + \frac{3 \cdot 5 \cdot \alpha}{2^6}\left(\frac{2^5 \hbar^2}{3^2 \cdot 5 \cdot \alpha m}\right)^{3/4}$$

$$= \frac{\hbar^2}{2m}\frac{3^{1/2}5^{1/4}\alpha^{1/4}m^{1/4}}{2^{5/4}\hbar^{1/2}} + \frac{3 \cdot 5 \cdot \alpha}{2^6}\frac{2^{15/4}\hbar^{3/2}}{3^{3/2}5^{3/4}\alpha^{3/4}m^{3/4}}$$

$$= \frac{3^{1/2}5^{1/4}\cdot\alpha^{1/4}\hbar^{3/2}}{2^{9/4}m^{3/4}} + \frac{5^{1/4}\alpha^{1/4}\hbar^{3/2}}{2^{9/4}3^{1/2}m^{3/4}}.$$

Multiplying and dividing the first term by $3^{1/2}$ gives us a common denominator, and

$$<\psi|\mathcal{H}|\psi>_{\min} = \frac{5^{1/4}\alpha^{1/4}\hbar^{3/2}}{2^{1/4}3^{1/2}m^{3/4}}\left(\frac{3+1}{4}\right) = \left(\frac{5\alpha\hbar^6}{2 \cdot 3^2 m^3}\right)^{1/4}$$

$$\boxed{\Rightarrow \quad E_0 \leq \left(\frac{5\alpha\hbar^6}{18m^3}\right)^{1/4}.}$$

Note for $V(x) = \alpha x^6$, α has dimensions of energy/length^6, so the dimensions of our result is energy, $i.e.$,

$$\left(\frac{5\alpha\hbar^6}{18m^3}\right)^{1/4} \rightarrow \left(\frac{E}{l^6}\frac{E^6 \cdot t^6}{m^3}\right)^{1/4} \rightarrow \left(\frac{E^7 \cdot t^6}{l^6 m^3}\right)^{1/4} \rightarrow \left(\frac{E^7}{E^3}\right)^{1/4} \rightarrow E,$$

which is consistent, as it must be.