Advanced Quantum Mechanics
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Part III: Approximation Methods in Quantum Mechanics

In your quantum mechanics courses last year, you explored perturbation theory: how to find approximate solutions for the quantum-mechanical behaviour of a system that is 'close to' an exactly soluble one. In this Part, we will examine some alternative approximate methods. We will cover two: the first provides a way of finding approximate ground states but is very widely applicable; the second assumes not that the perturbation is small, but that it is *slowly varying*.

3.1 The variational method

We now move to cover the first approximation scheme: the **variational method**. This method is more restricted than perturbation theory, in that it can only provide an approximation to the ground state wave function and energy; it has nothing to say about excited states. However, it is fairly universally applicable, so if the potential is not close to a solvable one it may be the only choice.

3.1.1 Variational theorem

The basic idea of the method is to guess a ground-state wave function, and then systematically improve that guess by tuning one or more parameters that the function contains. For example, if we guessed a Gaussian, we might tune its width. The way to tell whether we're improving our guess is to see whether our tuning is lowering the energy of the state. Since the ground-state is the lowest energy (normalised) state possible, if we're lowering the energy we must[1] be getting closer to the ground state.

Thus the method is founded on a theorem — the **variational theorem** — which says that the ground-state energy is the lowest value the expectation value of $\hat{H}$ can ever take, i.e. that for any normalised ket $|\psi\rangle$,

$$\langle\psi|\hat{H}|\psi\rangle \geqslant E_0, \tag{1}$$

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

Let us prove this theorem. We do so by decomposing $|\psi\rangle$ in terms of the eigenkets of $\hat{H}$:

$$|\psi\rangle = \sum_n c_n|n\rangle. \tag{2}$$

Since the ket $|\psi\rangle$ is normalised, we know that

$$\sum_n |c_n|^2 = 1. \tag{3}$$

[1] Actually, this isn't strictly true. We could be heading towards a local, but not a global, energy minimum, and thus be moving away from the ground state. This is an ever-present danger of the variational method, and one of its unattractive features.

Substituting (2) into the expectation value of $\hat{H}$, we find

$$\begin{aligned}
\langle\psi|\hat{H}|\psi\rangle &= \left(\sum_n c_n^*\langle n|\right)\hat{H}\left(\sum_m c_m|m\rangle\right) && (4)\\
&= \sum_{n,m} c_n^* c_m \langle n|\hat{H}|m\rangle && (5)\\
&= \sum_{n,m} c_n^* c_m E_m \underbrace{\langle n|m\rangle}_{=\delta_{nm}} && (6)\\
&= \sum_n |c_n|^2 E_n && (7)\\
&= E_0 \sum_n |c_n|^2 \frac{E_n}{E_0}. && (8)
\end{aligned}$$

Now, this looks a bit like the normalisation sum, except that we have an extra factor of E_n/E_0 in each term. This factor is clearly greater than or equal to one, since every eigenenergy is greater than or equal to the ground-state energy. Hence

$$\begin{aligned}
\langle\psi|\hat{H}|\psi\rangle &\geqslant E_0 \underbrace{\sum_n |c_n|^2}_{=1 \quad \text{(normalisation)}} && (9)\\
&= E_0, && (10)
\end{aligned}$$

which completes the proof.

3.1.2 Procedure

What this theorem really guarantees is that if we keep reducing the energy we can't 'overshoot', provided that the state is normalised. Thus the procedure of the variational method is as follows:

1. Guess a trial ground-state for the Hamiltonian of interest. (Make sure it's one you can do integrals with, otherwise it won't be much use!) Include one or more parameters that can be tuned to improve your guess.

2. Normalise the state. (This step is very important, since the variational theorem applies only to normalised states.)

3. Calculate the expectation value of $\hat{H}$ in your trial state.

4. Minimise that expectation value with respect to the parameter(s) you included in step 1.

The result is the best guess at the ground-state wave function, i.e. the member of your family of trial states that gets closest to the true ground-state energy.

3.1.3 Example

As an example, let us again take the harmonic oscillator. We shall guess a Gaussian as the ground-state wave function[2]:

$$\psi_\beta(x) = \left(\frac{2\beta}{\pi}\right)^{1/4} e^{-\beta x^2}. \tag{11}$$

Since I know the normalisation constant needed for a Gaussian, I have just written it down directly, thereby completing steps 1 and 2 in one go. The parameter β, which is related to the width of the Gaussian, is the one I'm going to be tuning to improve my guess.

Now we calculate the expectation value of the Hamiltonian in this state. The Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2; \tag{12}$$

let us calculate the expectation values of $\hat{T}$ and $\hat{V}$ separately, and then add them together.

The expectation value of the kinetic energy operator $\hat{T}$ is given by

$$\begin{aligned}
\langle\psi|\hat{T}|\psi\rangle &= \int_{-\infty}^{\infty} \psi_\beta^*(x)\hat{T}\psi_\beta(x)dx & (13)\\
&= -\frac{\hbar^2}{2m}\left(\frac{2\beta}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-\beta x^2}\frac{\partial^2}{\partial x^2}e^{-\beta x^2}dx. & (14)
\end{aligned}$$

The second derivative of the Gaussian is obtained as follows:

$$\begin{aligned}
\frac{\partial}{\partial x}e^{-\beta x^2} &= -2\beta x e^{-\beta x^2}; & (15)\\
\frac{\partial^2}{\partial x^2}e^{-\beta x^2} &= -2\beta\frac{\partial}{\partial x}\left(xe^{-\beta x^2}\right) & (16)\\
&= -2\beta\left(-2\beta x^2 e^{-\beta x^2} + e^{-\beta x^2}\right) & (17)\\
&= 4\beta^2 x^2 e^{-\beta x^2} - 2\beta e^{-\beta x^2}. & (18)
\end{aligned}$$

Substituting this into (14), we find

$$\langle\psi|\hat{T}|\psi\rangle = -\frac{\hbar^2}{2m}\left(\frac{2\beta}{\pi}\right)^{1/2}\left[4\beta^2\int_{-\infty}^{\infty} x^2 e^{-2\beta x^2}dx - 2\beta\int_{-\infty}^{\infty} e^{-2\beta x^2}dx\right]. \tag{19}$$

Using the standard Gaussian integrals

$$\begin{aligned}
\int_{-\infty}^{\infty} e^{-\alpha x^2}dx &= \sqrt{\pi}\alpha^{-1/2}; & (20)\\
\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2}dx &= \frac{1}{2}\sqrt{\pi}\alpha^{-3/2}, & (21)
\end{aligned}$$

[2] A fortuitous guess, since the true ground-state wave function is indeed a Gaussian! — normally we are not in a position to make such omniscient guesses.

we obtain

$$\begin{aligned}
\langle\psi|\hat{T}|\psi\rangle &= -\frac{\hbar^2}{2m}\left(\frac{2\beta}{\pi}\right)^{1/2}\left[2\beta^2\sqrt{\pi}(2\beta)^{-3/2} - 2\beta\sqrt{\pi}(2\beta)^{-1/2}\right] && (22)\\
&= -\frac{\hbar^2}{2m}\left[\beta - 2\beta\right] && (23)\\
&= \frac{\hbar^2\beta}{2m}. && (24)
\end{aligned}$$

The great thing about this part of the result is that it doesn't depend on the potential energy $V(x)$, which means that once you've calculated it once, you never have to do so again!

As for the potential energy,

$$\begin{aligned}
\langle\psi|\hat{V}|\psi\rangle &= \int_{-\infty}^{\infty}\psi_\beta^*(x)\hat{V}\psi_\beta(x)dx && (25)\\
&= \frac{1}{2}k\left(\frac{2\beta}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}e^{-\beta x^2}x^2e^{-\beta x^2}dx && (26)\\
&= \frac{1}{2}k\left(\frac{2\beta}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}x^2e^{-2\beta x^2}dx && (27)\\
&= \frac{1}{4}k\sqrt{\pi}\left(\frac{2\beta}{\pi}\right)^{1/2}(2\beta)^{-3/2} && (28)\\
&= \frac{k}{8\beta}, && (29)
\end{aligned}$$

where we have again used the standard Gaussian integral (21).

Thus the expectation value of the Hamiltonian is given by

$$\langle\psi|\hat{H}|\psi\rangle = \langle\psi|\hat{T}|\psi\rangle + \langle\psi|\hat{V}|\psi\rangle = \frac{\hbar^2\beta}{2m} + \frac{k}{8\beta}. \tag{30}$$

Minimising this with respect to β yields an equation for β_0, the value of β that minimises $\langle\hat{H}\rangle$:

$$\frac{\hbar^2}{2m} - \frac{k}{8\beta_0^2} = 0. \tag{31}$$

Rearranging this gives

$$\beta_0 = \frac{\sqrt{mk}}{2\hbar}, \tag{32}$$

which may be rewritten in terms of the classical frequency of the oscillator, $\omega = \sqrt{k/m}$, as

$$\beta_0 = \frac{m\omega}{2\hbar}. \tag{33}$$

Substituting this back into (30), we obtain

$$\begin{aligned}
\langle\psi|\hat{H}|\psi\rangle &= \frac{\hbar^2\beta_0}{2m} + \frac{k}{8\beta_0} && (34)\\
&= \frac{\hbar^2}{2m}\frac{m\omega}{2\hbar} + \frac{m\omega^2}{8}\frac{2\hbar}{m\omega} && (35)\\
&= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} && (36)\\
&= \frac{\hbar\omega}{2}. && (37)
\end{aligned}$$

This is, of course, the exact ground state of SHO1. That's not surprising, since in this case our family of trial wave functions included the exact ground state wave function — we are not usually so lucky!

3.2 The Wentzel-Kramers-Brillouin (WKB) method

We now explore the 'WKB' method which allows us to explore slowly time-varying problems.

3.2.1 Basic idea

A classical particle subject to no forces (i.e. in a constant potential $V(x) = V_0$) obeys Newton's First Law: it moves in a straight line with constant speed. Since

$$\frac{d\mathbf{p}}{dt} = \mathbf{0}, \tag{38}$$

its momentum is conserved. The quantum equivalent of this is the statement that the eigenstates of a free particle are eigenstates of the momentum operator — hence we label them by the value that the momentum takes, $|\mathbf{p}\rangle$. The wave function in such a momentum eigenstate is given by the usual plane-wave form,

$$\psi(x) \equiv \langle x|p\rangle = A \exp\left(\frac{ipx}{\hbar}\right), \tag{39}$$

where A is some normalisation that we don't care too much about, and for simplicity we assume that the particle moves in one dimension.

Now, what about a classical particle that is subject only to weak forces (i.e. slowly varying potentials)? Its motion will be quite close to that described by Newton's First Law, with only gentle deviations: speeding up a bit as it comes into a region of low potential, or slowing down a bit as it comes into a region of high potential. Thus we might imagine that the corresponding quantum wave function would be 'quite close' to a plane wave,

$$\psi(x) \approx A \exp\left(\frac{i}{\hbar}\int_{x_0}^{x} p(x')dx'\right), \tag{40}$$

where we take the position-dependent momentum (called the **orbit** of the particle) from the corresponding classical problem (i.e. $p(x)$ is the particle's **classical orbit**). The easiest way to determine the classical orbit is usually using conservation of energy:

$$E = \frac{p^2}{2m} + V(x) \qquad \rightarrow \qquad p(x) = \pm\sqrt{2m\,(E - V(x))}. \tag{41}$$

For most practical purposes we choose the positive value of the square root.

The integral in (40) is taken from some reference position x_0, which is arbitrary. Notice that if we remove the external forces, $p(x)$ becomes a constant p, and the integral gives px, in agreement with (39). (40) is referred to as the **zeroth-order WKB approximation**, after Wentzel, Kramers, and Brillouin, who investigated this approach in the early days of quantum mechanics.

3.2.2 Bound states and quantisation

A special case arises if the classical orbit is closed. This happens when, in some region of space, $V(x) > E$. In that region, according to (41), the momentum becomes imaginary. This

imaginary momentum, substituted into (40), produces a decaying exponential — exactly the form that we know the wave function does take in classically forbidden regions!

The fact that the orbit is closed produces another requirement: *single-valuedness* of the wave function. Look again at (40). If the orbit is closed, we can do the integral

$$\int_{x_0}^{x} p(x')dx' \tag{42}$$

in more than one way. We could just go directly from x_0 to x; alternatively, we could start at x_0, complete a whole orbit, and then after that proceed from x_0 to x. Which choice we make shouldn't make any difference to the value of $\psi(x)$. We guarantee this provided that the contribution from the whole orbit is an integer multiple of $2\pi\hbar$, since $e^{2i\pi} = 1$. So for closed orbits it seems we must demand that

$$\oint p(x)dx = 2\pi\hbar n, \tag{43}$$

where n is an integer. Actually this isn't quite right, because the 'leaking' of the wave function into the classically forbidden regions affects things. The correct form is actually

$$\oint p(x)dx = 2\pi\hbar\left(n + \gamma\right), \tag{44}$$

where γ is called the **Maslov index**. The condition (44) is called the **WKB quantisation condition**, and may be used to determine the allowed energies of the quantum eigenstates of the problem. Notice that the integral on the left-hand side is nothing but the area enclosed by the classical orbit in phase space[3].

3.2.3 Example: the harmonic oscillator

As an example of the method, consider the harmonic oscillator, for which the potential is given by

$$V(x) = \frac{1}{2}kx^2, \tag{45}$$

where k is the spring constant. To find the classical orbits, we use conservation of energy:

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2. \tag{46}$$

This is the equation of an ellipse in phase space — see Fig. 1. The turning points x_c (i.e. the maximum distance from the origin for a classical particle) are the points at which $p = 0$, i.e.

$$E = \frac{1}{2}kx_c^2 \qquad \rightarrow \qquad x_c = \pm\sqrt{\frac{2E}{k}}. \tag{47}$$

Notice that we know which way round the orbit it goes: when the momentum is positive (in the upper half of phase space), it must be moving in the positive x-direction (i.e. to the right).

[3]Phase space is defined as the two-dimensional space with position, x, on one axis, and momentum, p, on the other.

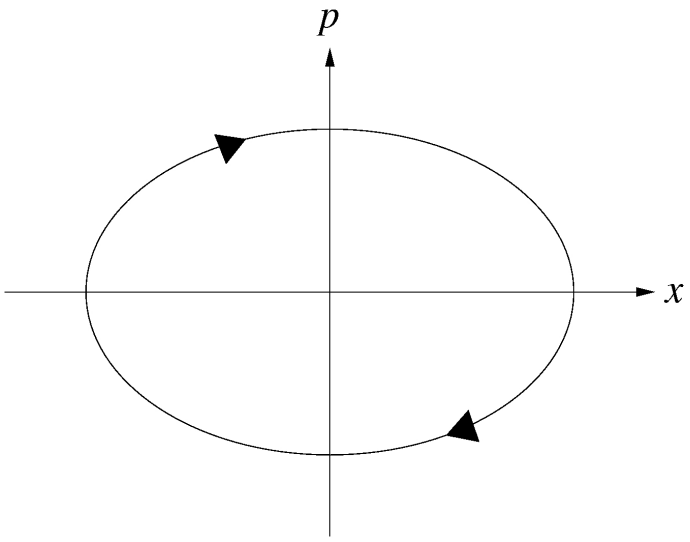

Figure 1: The classical orbit of a simple harmonic oscillator.

The zeroth-order WKB wave function is given by (40). To evaluate the integral, let's take the reference point to be zero. Then

$$\int_0^x p(x')dx' = \int_0^x \sqrt{2mE - mk(x')^2}\, dx' \tag{48}$$

$$= \sqrt{2mE}\int_0^x \sqrt{1 - \frac{k}{2E}(x')^2}\, dx'. \tag{49}$$

Now let us write

$$x' = x_c z = z\sqrt{\frac{2E}{k}}; \tag{50}$$

with this substitution, the integral becomes

$$\int_0^x p(x')dx' = \sqrt{2mE}\sqrt{\frac{2E}{k}}\int_0^{x/x_c} \sqrt{1 - z^2}\, dz. \tag{51}$$

This integral can be completed if desired, but the result is not especially enlightening. Substituting this back into (40) gives the zeroth-order WKB approximation to the harmonic oscillator wave functions.

The more interesting bit is the quantisation condition (44). (All orbits of a simple harmonic oscillator are closed, so this quantisation condition must be applied irrespective of the energy E.) Since the orbit in phase space is just an ellipse, the integral on the left-hand side of (44) is just the area enclosed by an ellipse. But this is given by πab, where a and b are the major and minor radii. Hence

$$\oint p(x)dx = \pi p_{\max} x_{\max} = \pi\sqrt{2mE}\sqrt{\frac{2E}{k}} = 2\pi E\sqrt{\frac{m}{k}}. \tag{52}$$

Hence the quantisation condition reads

$$2\pi E\sqrt{\frac{m}{k}} = 2\pi\hbar\,(n+\gamma)\,; \tag{53}$$

rearranging this, we obtain

$$E = \hbar\sqrt{\frac{k}{m}}\,(n+\gamma)\,. \tag{54}$$

We recognise the factor $\sqrt{k/m}$ as the classical angular frequency of the oscillator. Calling this ω as usual, the quantisation condition becomes

$$E = \hbar\omega\,(n+\gamma)\,. \tag{55}$$

Given that the Maslov index for this problem is $1/2$ (which can be proved, though we don't have time to do so here), this becomes

$$E = \hbar\omega\left(n+\frac{1}{2}\right); \tag{56}$$

rather impressively, the WKB approximation has got the energy spectrum of the one-dimensional simple harmonic oscillator *exactly right*!