1 Perturbation Theory

The set of quantum mechanical problems which admit exact analytical solutions is very small. Fortunately, there exists a powerful method for achieving approximate solutions to a much wider class of problems, based on perturbing away from known exact results. This method is **perturbation theory**. In this lecture we will consider the simplest case of **time-independent** perturbations in which all energies remain **non-degenerate**. We will deal with these more general cases in subsequent lectures.

We begin by assuming we can solve exactly for a complete set of n eigenvalues $E_n^{(0)}$ and eigenfunctions $\psi_n^{(0)}(x)$ of a given time independent Schrödinger equation

$$\hat{H}_0\psi_n^{(0)}(x) = E_n^{(0)}\psi_n^{(0)}(x). \tag{1}$$

The superscript 0 indicates that this is the unperturbed case. We then perturb the Hamiltonian according to

$$\hat{H}_0 \rightarrow \hat{H} = \hat{H}_0 + \hat{H}' \tag{2}$$

and seek an approximate solution for the eigenvalues E_n and eigenfunctions ψ_n

$$\hat{H}\psi_n(x) = E_n\psi_n(x). \tag{3}$$

A convenient trick at this point is to define

$$\hat{H}' = \lambda\hat{V} \tag{4}$$

where λ is a dimensionless real parameter. In this way, setting $\lambda = 0$ returns the unperturbed problem which we know how to solve. Setting $\lambda = 1$ instead gives the perturbed problem. Provided no energy levels cross in the interval $\lambda \in [0, 1]$ it is safe to assume that the two sets of solutions can be smoothly connected.

We seek solutions to

$$\left(\hat{H}_0 + \lambda\hat{V}\right)\psi_n(\lambda, x) = E_n(\lambda)\,\psi_n(\lambda, x). \tag{5}$$

Our **key assumption** is that the solutions to the full equation are close enough to those of the unperturbed case that we are justified in expanding the behaviour in λ as a Taylor series:

$$\psi_n(\lambda, x) = \sum_{m=0}^{\infty}\lambda^m\psi_n^{(m)}(x) = \psi_n^{(0)}(x) + \lambda\psi_n^{(1)}(x) + \lambda^2\psi_n^{(2)}(x) + \ldots \tag{6}$$

$$E_n(\lambda) = \sum_{m=0}^{\infty}\lambda^m E_n^{(m)} = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \tag{7}$$

Substituting the trial solutions of Eqs. 6 and 7 into Eq. 5 we can proceed to a solution working power-by-power in λ:

$$\lambda^0: \quad \hat{H}_0\psi_n^{(0)}(x) = E_n^{(0)}\psi_n^{(0)}(x) \tag{8}$$

$$\lambda^1: \quad \hat{H}_0\psi_n^{(1)}(x) + \hat{V}\psi_n^{(0)}(x) = E_n^{(0)}\psi_n^{(1)}(x) + E_n^{(1)}\psi_n^{(0)}(x) \tag{9}$$

$$\lambda^2: \quad \hat{H}_0\psi_n^{(2)}(x) + \hat{V}\psi_n^{(1)}(x) = E_n^{(0)}\psi_n^{(2)}(x) + E_n^{(1)}\psi_n^{(1)}(x) + E_n^{(2)}\psi_n^{(0)}(x) \tag{10}$$

$$\vdots$$

Note that the expansion parameter λ is best thought of as a bookkeeping device introduced to keep track of the order of the perturbation. The sums defined in Eqs. 6 and 7 are not in general convergent even for $0 \leq \lambda < 1$. Instead, they are asymptotic, meaning they converge for a few terms before diverging. We will ultimately set $\lambda = 1$.

1.1 First-order energy shift

The λ^0 equation (Eq. 8) is simply the unperturbed Schrödinger equation which we can solve exactly (Eq. 1). The first correction is found in the λ^1 terms (Eq. 9). We'd first like to solve for $E_n^{(1)}$, the first-order shift in the n^{th} energy coming from the perturbation. We can re-arrange the λ^1 equation to the form

$$E_n^{(1)}\psi_n^{(0)}(x) = \hat{V}\psi_n^{(0)}(x) + \left(\hat{H}_0 - E_n^{(0)}\right)\psi_n^{(1)}(x). \tag{11}$$

To isolate $E_n^{(1)}$ on the left, we can use the fact that the eigenfunctions $\psi_n^{(0)}(x)$ form an orthonormal basis, such that

$$\int \psi_n^{(0)*}(x)\,\psi_m^{(0)}(x)\,\mathrm{d}x = \delta_{nm} \tag{12}$$

with δ_{nm} the Kronecker delta. Left-multiplying Eq.11 by $\psi_n^{(0)*}$ and integrating over the relevant domain gives

$$E_n^{(1)}\int \psi_n^{(0)*}(x)\,\psi_n^{(0)}(x)\,\mathrm{d}x = \int \psi_n^{(0)*}(x)\,\hat{V}\psi_n^{(0)}(x)\,\mathrm{d}x + \int \psi_n^{(0)*}(x)\left(\hat{H}_0 - E_n^{(0)}\right)\psi_n^{(1)}(x)\,\mathrm{d}x. \tag{13}$$

The final term on the right-hand side vanishes, since we can act to the left with $\hat{H}_0$ and use the λ^0 result:

$$\psi_n^{(0)*}(x)\left(\hat{H}_0 - E_n^{(0)}\right) = \psi_n^{(0)*}(x)\left(E_n^{(0)} - E_n^{(0)}\right) = 0. \tag{14}$$

Re-arranging Eq.13 then gives the result

$$E_n^{(1)} = \int \psi_n^{(0)*}(x)\,\hat{V}\psi_n^{(0)}(x)\,\mathrm{d}x. \tag{15}$$

We can now formally identify the first-order correction to the original problem by setting $\lambda = 1$, for which $\hat{V} = \hat{H}'$, giving the final result:

$$\boxed{E_n^{(1)} = \int \psi_n^{(0)*}(x)\,\hat{H}'\psi_n^{(0)}(x)\,\mathrm{d}x.} \tag{16}$$

The shift in the n^{th} energy level induced by $\hat{H}'$, found to first order in perturbation theory, is simply the expectation value of $\hat{H}'$ evaluated with the unperturbed n^{th} eigenstate.

Example: the anharmonic oscillator

The anharmonic oscillator is described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \epsilon a^{-4}\hat{x}^4 \tag{17}$$

with $a = \sqrt{\frac{\hbar}{m\omega}}$ and ϵ a real parameter with the dimensions of energy. We can define

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

with

$$\begin{aligned} \hat{H}_0 &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \\ \hat{H}' &= \epsilon a^{-4}\hat{x}^4 \end{aligned} \tag{18}$$

where $\hat{H}_0$ is the standard quantum harmonic oscillator, whose (normalized) eigenstates and energies are given by:

$$\begin{aligned} E_n^{(0)} &= \hbar\omega\left(n + \frac{1}{2}\right) \\ \psi_0^{(0)}(x) &= \left(\frac{1}{\pi a^2}\right)^{1/4}\exp\left(-\frac{x^2}{2a^2}\right) \\ \psi_{n+1}^{(0)}(x) &= \frac{1}{\sqrt{n+1}}\frac{1}{\sqrt{2}a}\left(x - a^2\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi_n^{(0)}(x). \end{aligned} \tag{19}$$

Using the result of Eq. 16 we find that the first-order energy shift is given by

$$E_n^{(1)} = \epsilon a^{-4}\int_{-\infty}^{\infty}\psi_n^{(0)*}(x)\,x^4\psi_n^{(0)}(x)\,\mathrm{d}x. \tag{20}$$

For example, the shift in the ground state energy is given by

$$\begin{aligned} E_0^{(1)} &= \epsilon a^{-4}\left(\frac{1}{\pi a^2}\right)^{1/2}\int_{-\infty}^{\infty}x^4\exp\left(-\frac{x^2}{a^2}\right)\mathrm{d}x \\ &\quad\downarrow \text{let } y = x/a \\ &= \epsilon\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}y^4\exp\left(-y^2\right)\mathrm{d}y \\ &= \frac{3}{4}\epsilon. \end{aligned}$$

Historical background: Erwin Schrödinger introduced perturbation theory as part of his wave mechanics approach in a 1926 paper. He attributed the technique to Lord Rayleigh (John William Strutt, 3rd Baron Rayleigh) who had employed it for the study of sound waves as introduced in his 1877 textbook *The Theory of Sound*. The technique is sometimes still referred to as Rayleigh-Schrödinger perturbation theory.

Rayleigh

1.2 First-order wavefunction shift

The first-order shift in the eigenstates is given by $\psi_n^{(1)}(x)$. To get this in terms of known quantities we can use the fact that $\psi_n^{(0)}$ comprise a complete set of basis states, and therefore any function (including $\psi_n^{(1)}(x)$) can be written in terms of them. Specifically

$$\psi_n^{(1)}(x) = \sum_m C_{nm}\psi_m^{(0)}(x) \tag{21}$$

$$= \sum_{m\neq n} C_{nm}\psi_m^{(0)}(x) + C_{nn}\psi_n^{(0)}(x) \tag{22}$$

where

$$C_{nm} = \int \psi_m^{(0)*}(x)\,\psi_n^{(1)}(x)\,\mathrm{d}x. \tag{23}$$

In fact, since both the unperturbed states $\psi_n^{(0)}(x)$ and the perturbed states $\psi_n(x)$ must be normalized we must have that $C_{nn} = 0$ to first order in λ.

Exercise 1: prove this result [solution at the end of the document].

We therefore have that

$$\psi_n^{(1)}(x) = \sum_{m\neq n} C_{nm}\psi_m^{(0)}(x). \tag{24}$$

To find C_{nm} we can return to Eq. 11, this time multiplying from the left with $\psi_m^{(0)*}(x)$ and integrating over x:

$$E_n^{(1)}\int \psi_m^{(0)*}(x)\,\psi_n^{(0)}(x)\,\mathrm{d}x = \int \psi_m^{(0)*}(x)\,\hat{V}\psi_n^{(0)}(x)\,\mathrm{d}x + \int \psi_m^{(0)*}(x)\left(E_m^{(0)} - E_n^{(0)}\right)\psi_n^{(1)}(x)\,\mathrm{d}x.$$

When $m = n$ this simply returns the result of the first-order energy shift. Considering instead the case $m \neq n$ gives

$$\int \psi_m^{(0)*}(x)\,\psi_n^{(1)}(x)\,\mathrm{d}x = C_{nm} = \frac{\int \psi_m^{(0)*}(x)\,\hat{V}\psi_n^{(0)}(x)\,\mathrm{d}x}{E_n^{(0)} - E_m^{(0)}}. \tag{25}$$

Substituting Eq. 25 into Eq. 24 gives

$$\psi_n^{(1)}(x) = \sum_{m\neq n} \frac{\int \psi_m^{(0)*}(y)\,\hat{V}\psi_n^{(0)}(y)\,\mathrm{d}y}{E_n^{(0)} - E_m^{(0)}}\psi_m^{(0)}(x)$$

and once again we formally set $\lambda = 1$, so that $\hat{V} = \hat{H}'$, to give the final result:

$$\boxed{\psi_n^{(1)}(x) = \sum_{m\neq n} \frac{\int \psi_m^{(0)*}(y)\,\hat{H}'\psi_n^{(0)}(y)\,\mathrm{d}y}{E_n^{(0)} - E_m^{(0)}}\psi_m^{(0)}(x)\,.} \tag{26}$$

1.3 Second-order energy shift

If perturbation theory is valid and useful for the problem at hand, we should only need to consider the first few terms. Higher order results can nevertheless be inferred by iterating the same processes as above. For example, to find the second-order correction to the energy we can start from the λ^2 result in Eq. 10, which re-arranges to:

$$\left(\hat{H}_0 - E_n^{(0)}\right)\psi_n^{(2)}(x) + \left(\hat{V} - E_n^{(1)}\right)\psi_n^{(1)}(x) = E_n^{(2)}\psi_n^{(0)}(x)\,. \tag{27}$$

As before, we can act from the left with $\psi_n^{(0)*}(x)$ and integrate over x to give

$$\int \psi_n^{(0)*}(x)\left(\hat{V} - E_n^{(1)}\right)\psi_n^{(1)}(x)\,\mathrm{d}x = E_n^{(2)}. \tag{28}$$

We can now substitute Eq. 26 for the first-order wavefunction correction $\psi_n^{(1)}(x)$, and set $\lambda = 1$ so that $\hat{V} = \hat{H}'$, to give the result

$$\boxed{E_n^{(2)} = \sum_{m\neq n} \frac{\int \psi_n^{(0)*}(x)\,\hat{H}'\psi_m^{(0)}(x)\,\mathrm{d}x \int \psi_m^{(0)*}(y)\,\hat{H}'\psi_n^{(0)}(y)\,\mathrm{d}y}{E_n^{(0)} - E_m^{(0)}}.} \tag{29}$$

1.4 Streamlining with Dirac notation*

*If you are familiar with Dirac notation, the working above can be carried out more elegantly. If not, this section can safely be skipped.

Defining the eigenkets

$$\langle x|n_i\rangle = \psi_n^{(i)}(x)$$

for $i = 0,\ 1,\ 2, \ldots$ we have

$$\hat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle \tag{30}$$

and we can rewrite Eqs. 5, 6, and 7 as

$$\left(\hat{H}_0 + \lambda\hat{V}\right)\left(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \ldots\right) = \left(E^{(0)} + \lambda E^{(1)} + \ldots\right)\left(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \ldots\right). \tag{31}$$

Once again equating powers of λ we obtain

$$\lambda^0: \quad \hat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle \tag{32}$$

$$\lambda^1: \quad \hat{H}_0|n^{(1)}\rangle + \hat{V}|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle \tag{33}$$

$$\lambda^2: \quad \hat{H}_0|n^{(2)}\rangle + \hat{V}|n^{(1)}\rangle = E_n^{(0)}|n^{(2)}\rangle + E_n^{(1)}|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle. \tag{34}$$

$$\vdots$$

To find the first order energy shift we re-arrange Eq. 33

$$E_n^{(1)}|n^{(0)}\rangle = \left(\hat{H}_0 - E_n^{(0)}\right)|n^{(1)}\rangle + \hat{V}|n^{(0)}\rangle \tag{35}$$

then left-multiply by $\langle n^{(0)}|$:

$$E_n^{(1)}\langle n^{(0)}|n^{(0)}\rangle = \langle n^{(0)}|\hat{H}_0 - E_n^{(0)}|n^{(1)}\rangle + \langle n^{(0)}|\hat{V}|n^{(0)}\rangle. \tag{36}$$

We have that $\langle n^{(0)}|\hat{H}_0 = \langle n^{(0)}|E_n^{(0)}$, and $\langle n^{(0)}|n^{(0)}\rangle = 1$. Using these results, and formally setting $\lambda = 1$ such that $\hat{V} = \hat{H}'$ gives the result

$$\boxed{E_n^{(1)} = \langle n^{(0)}|\hat{V}|n^{(0)}\rangle.} \tag{37}$$

To find the first-order shift in the eigenstate we return to Eq. 33, re-arranged as follows:

$$\left(\hat{H}_0 - E_n^{(0)}\right)|n^{(1)}\rangle = \left(E_n^{(1)} - \hat{V}\right)|n^{(0)}\rangle. \tag{38}$$

Acting from the left with $\langle m^{(0)}|$, where $m \neq n$, gives

$$\left(E_m^{(0)} - E_n^{(0)}\right)\langle m^{(0)}|n^{(1)}\rangle = -\langle m^{(0)}|\hat{V}|n^{(0)}\rangle \tag{39}$$

and so

$$\langle m^{(0)}|n^{(1)}\rangle = \frac{\langle m^{(0)}|\hat{V}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} \quad (m \neq n)\,. \tag{40}$$

Using the resolution of the identity:

$$\mathbb{I} = \sum_m |m^{(0)}\rangle\langle m^{(0)}| \tag{41}$$

we can write

$$|n^{(1)}\rangle = \sum_m |m^{(0)}\rangle\langle m^{(0)}|n^{(1)}\rangle \tag{42}$$

and inserting Eq. 40 (with $\lambda = 1$) gives the result

$$\boxed{|n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle m^{(0)}|\hat{H}'|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}|m^{(0)}\rangle.} \tag{43}$$

1.5 Summary and Further Reading

In this lecture we saw how to find an approximate solution for the eigenfunctions and energy levels of a quantum system, by perturbing a system for which we can obtain an exact result.

Starting from an unperturbed Hamiltonian $\hat{H}_0$ for which we have the exact energy eigenvalues $E_n^{(0)}$ and normalized eigenfunctions $\psi_n^{(0)}(x)$:

$$\hat{H}_0\psi_n^{(0)}(x) = E_n^{(0)}\psi_n^{(0)}(x)$$

and perturbing to a new Hamiltonian $\hat{H}_0 \to \hat{H} = \hat{H}_0 + \hat{H}'$ such that

$$\hat{H}\psi_n(x) = E_n\psi_n(x)$$

with

$$\psi_n(x) = \sum_{m=0}^{\infty} \psi_n^{(m)}(x)$$
$$E_n = \sum_{m=0}^{\infty} E_n^{(m)}$$

we found expressions for the following:

- the first-order correction to the energy:

$$E_n^{(1)} = \int \psi_n^{(0)*}(x)\,\hat{H}'\psi_n^{(0)}(x)\,\mathrm{d}x$$

- the first-order correction to the wavefunction:

$$\psi_n^{(1)}(x) = \sum_{m\neq n} \frac{\int \psi_m^{(0)*}(y)\,\hat{H}'\psi_n^{(0)}(y)\,\mathrm{d}y}{E_n^{(0)} - E_m^{(0)}}\psi_m^{(0)}(x)$$

- the second-order correction to the energy

$$E_n^{(2)} = \sum_{m\neq n} \frac{\int \psi_n^{(0)*}(x)\,\hat{H}'\psi_m^{(0)}(x)\,\mathrm{d}x \int \psi_m^{(0)*}(y)\,\hat{H}'\psi_n^{(0)}(y)\,\mathrm{d}y}{E_n^{(0)} - E_m^{(0)}}.$$

We also saw how to arrive at these results more succinctly using Dirac notation.

Perturbation theory allows the solution of a number of physically interesting problems which do not admit an exact solution. Some examples include: a spin in a transverse magnetic field; the splitting of atomic spectral lines in an applied electric field (the quadratic Stark effect); and the Van der Waals interaction between two Hydrogen atoms.

For further reading, a good reference is provided by J. J. Sakurai, *Modern Quantum Mechanics* (Ed. San Fu Tuan, Addison Wesley (New York) 1994).

1.6 Solutions to Exercises

Exercise 1

Given that we can write

$$\psi_n^{(1)}(x) = \sum_{m \neq n} C_{nm}\psi_m^{(0)}(x) + C_{nn}\psi_n^{(0)}(x)$$

with

$$C_{nm} = \int \psi_m^{(0)*}\psi_n^{(1)}(x)\,\mathrm{d}x$$

and since both $\psi_n(x)$ and $\psi_n^{(0)}(x)$ are normalized, we are asked to show that C_{nn} must equal zero to first order in λ. We have that

$$\psi_n(x) = \psi_n^{(0)}(x) + \lambda\psi_n^{(1)}(x)$$

and the normalization of $\psi_n(x)$ tells us that

$$\begin{aligned}
1 &= \int \psi_n^*(x)\,\psi_n(x)\,\mathrm{d}x \\
&= \int \left(\psi_n^{(0)*}(x) + \lambda\psi_n^{(1)*}(x)\right)\left(\psi_n^{(0)}(x) + \lambda\psi_n^{(1)}(x)\right)\mathrm{d}x \\
&= \int \psi_n^{(0)*}(x)\,\psi_n^{(0)}(x)\,\mathrm{d}x + \lambda\int \psi_n^{(0)*}(x)\,\psi_n^{(1)}(x)\,\mathrm{d}x + \lambda\int \psi_n^{(1)*}(x)\,\psi_n^{(0)}(x)\,\mathrm{d}x + \mathcal{O}\left(\lambda^2\right).
\end{aligned}$$

Since $\psi_n^{(0)}(x)$ is also normalized, the first term on the right-hand side is equal to one. Using the definition of C_{nm} above, it follows that

$$0 = C_{nn} + C_{nn}^*.$$

As we are free to choose the overall phase of the wavefunction we can always choose C_{nn} to be real, and so it must be equal to zero.