

Perturbation Theory

What is meant by the term perturbation?

A perturbation is a small change in our description of a system, which we might split into two possibilities

1. That we have an approximation description which we might want to make better. For example, suppose we have described the hydrogen atom in terms of the electrostatic interaction between the electron and the nucleus (proton). For a better description we might also want to include the magnetic interaction between the magnetic moment (spin) of the electron and the magnetic field that the electron perceives due to the motion of the electron through the electric field caused by the nucleus. (This is spin orbit coupling, see lecture notes on that topic.)
2. That we have a good approximation of the system, but want to add the effects of an external influence. For example we might have a good description of an isolated atom, but want to know what happens when it is placed in an external magnetic field. (This is the Zeeman effect, see lecture notes on that topic.)

In this class we shall be using perturbation theory to develop an idea of atomic and molecular energies, and so will be using a quantum mechanical description of perturbation theory. However, note that perturbation theory is not restricted to just quantum mechanics. The first use of perturbation theory had nothing to do with quantum mechanics at all, it preceded quantum mechanics by many years. It was first used to describe the motion of the planets, for which the gravitational attraction between each planet and the Sun is dominant, but for which better results are obtained if the gravitational attraction between planets is also included.

There is one important point to consider. When the perturbation is included the equations are usually unsolvable, and approximation techniques have to be employed. These approximations will be poor if the perturbation is large. The best results are always obtained when the initial approximation is very good and only a small correction has to be made.

Schrodinger's Equation for an unperturbed system

Suppose we have a system which is described by the Hamiltonian H_0 , with wave functions (eigenfunctions) and energies (eigenvalues) ψ_n and E_n , where $1 \leq n \leq \infty$. Schrodinger's equation is then

$$H_0 \psi_n = E_n \psi_n$$

we shall assume that this equation is solvable, that is we know each one of the energies E_n and each one of the wave functions ψ_n . Knowing them will allow us (in principle) to make the corrections required to account for a perturbation.

Schrodinger's Equation for the perturbed system

Now apply a perturbation H' to the system, so that the Hamiltonian changes from H_0 to a new Hamiltonian given by $H = H_0 + H'$. Because the Hamiltonian has changed then the wave functions must change also. Let them be written as ψ'_n . The energies also change. Let them be written as E'_n . Schrodinger's equation now becomes

$$H \psi'_n = (H_0 + H') \psi'_n = E'_n \psi'_n$$

Commonly the problem with this equation is that it cannot be solved directly even when the full Hamiltonian is known. In order to get a solution (even an approximate one) we have to resort to perturbation theory.

An overview of the method

Without an analytical method of solving the equation for the perturbed system we have to rely on approximation methods. This can involve successive approximation getting a better and better solution until one of sufficient accuracy is found.

1. Using the known initial energies and wave functions we will calculate a better approximation to the energies. (First order perturbation theory)
2. Using the improved energies and the initial wave functions we will calculate better wave functions.
3. Using the improved energies and improved wave functions we will calculate even better approximation to the energies. (Second order perturbation theory)
4. Using the improved energies and the improved wave functions we will calculate even better wave functions.
5. Repeat as necessary.

For this class the first step (First order perturbation theory) is sufficient to illustrate the concept.

First order perturbation theory - An approximate solution

A first order approximation to the second of these equations can be found by making two substitutions

1. $E'_n = E_n + \Delta E_n$, with the approximation that $\Delta E_n \ll E_n$ for all values of n .
2. $\psi'_n = \sum a_{nm} \psi_m$, where the summation is over all possible values of m . We will make a second approximation here, that to a first approximation the perturbation does not significantly alter the wave functions, and so $a_{nn} \approx 1$ and $a_{nm} \approx 0$ for all values of $m \neq n$. With this approximation we shall set $\psi_n = \psi'_n$.

Substituting into Schrodinger's equation we get

$$(H_0 + H') \psi_n = (E_n + \Delta E_n) \psi_n$$

If we now subtract off Schrodinger's equation for the unperturbed system we are left with

$$H' \psi_n = \Delta E_n \psi_n$$

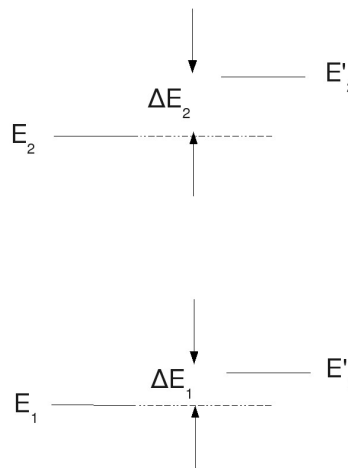
To extract ΔE_n from this equation, multiply by ψ_n^* and integrate over all space. The result is

$$\Delta E_n = \frac{\int \psi_n^* H' \psi_n dv}{\int \psi_n^* \psi_n dv} = \int \psi_n^* H' \psi_n dv$$

Where we have used the normalization condition to set the denominator to 1.

Result

We now have an approximation (often a good approximation) which shows that the energy of the level n is shifted by a small amount which depends on the strength of the approximation and on the wave function. The result is illustrated in figure 1.



Splitting of degenerate energy levels

A degeneracy occurs when ever there are two (or more) energy levels with the same energy, that is

$$E_m = E_n = E_p = E_q = \dots\dots$$

for some values of m, n, p, q , etc. For example, if we take the $n=2$ level of hydrogen, using the Coulombic potential energy between the electron and the proton as the only potential energy term in Schroedinger's equation, then there are eight possible wave functions with the same energy (see table to right).

However, the wave functions which correspond to the degenerate level are all different, and it is quite likely that the integral used to determine each value of ΔE_n will be different. In that case the perturbed energies will be different. We say that the perturbation has lifted the degeneracy. This is illustrated in figure 2 for a three-fold degenerate level of the unperturbed system, which becomes three separate energy levels once the perturbation is applied.

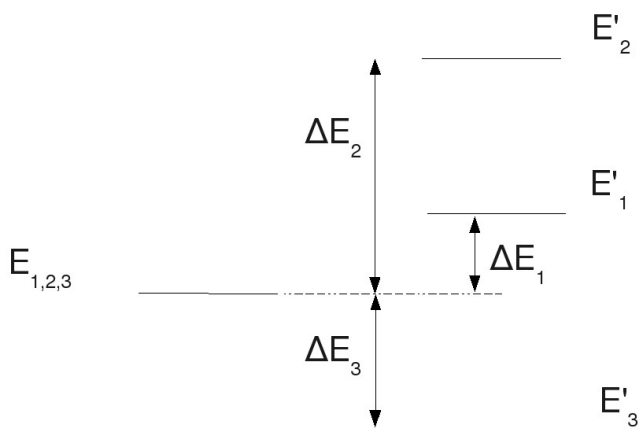


Figure 1

| n | l | m_l | s | m_s |
|-----|-----|-------|---------------|----------------|
| 2 | 0 | 0 | $\frac{1}{2}$ | $-\frac{1}{2}$ |
| 2 | 0 | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ |
| 2 | 1 | -1 | $\frac{1}{2}$ | $-\frac{1}{2}$ |
| 2 | 1 | -1 | $\frac{1}{2}$ | $\frac{1}{2}$ |
| 2 | 1 | 0 | $\frac{1}{2}$ | $-\frac{1}{2}$ |
| 2 | 1 | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ |
| 2 | 1 | 1 | $\frac{1}{2}$ | $-\frac{1}{2}$ |
| 2 | 1 | 1 | $\frac{1}{2}$ | $\frac{1}{2}$ |

The quantum numbers of the eight wave functions of the degenerate $n=2$ level of hydrogen

Figure 2