

SECOND ORDER NON-DEGENERATE PERTURBATION THEORY

Link to: [physicspages home page](#).

To leave a comment or report an error, please use the [auxiliary blog](#).

References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.4.

We can get the second order perturbation to the energy by starting with the coefficients of λ^2 in the equation:

$$(1) \quad (H_0 + \lambda V) (\psi_{n0} + \lambda \psi_{n1} + \lambda^2 \psi_{n2} + \dots) = (E_{n0} + \lambda E_{n1} + \lambda^2 E_{n2} + \dots) (\psi_{n0} + \lambda \psi_{n1} + \lambda^2 \psi_{n2} + \dots)$$

This gives us

$$(2) \quad H_0 \psi_{n2} + V \psi_{n1} = E_{n0} \psi_{n2} + E_{n1} \psi_{n1} + E_{n2} \psi_{n0}$$

Using the bra-ket notation $\psi_{ni} = |ni\rangle$, we can multiply both sides by $\langle n0|$ and get

$$(3) \quad \langle n0|H_0|n2\rangle + \langle n0|V|n1\rangle = \langle n0|E_{n0}|n2\rangle + \langle n0|E_{n1}|n1\rangle + \langle n0|E_{n2}|n0\rangle$$

Since H_0 is hermitian, we can swap it to the bra end in the first term and then use $\langle H_0 n0| = E_{n0}$, and since the E_{ni} s are just constants, they come out of the brackets on the right, and since $|n0\rangle$ is normalized, we get

$$(4) \quad E_{n0} \langle n0|n2\rangle + \langle n0|V|n1\rangle = E_{n0} \langle n0|n2\rangle + E_{n1} \langle n0|n1\rangle + E_{n2}$$

$$(5) \quad \langle n0|V|n1\rangle = E_{n1} \langle n0|n1\rangle + E_{n2}$$

We worked out $|n1\rangle$ when analyzing first order perturbation theory, and we got

$$(6) \quad |n1\rangle = \sum_{j \neq n} \frac{\langle j0|V|n0\rangle}{E_{n0} - E_{j0}} |j0\rangle$$

Since the unperturbed wave functions form an orthonormal set, $\langle n0|j0\rangle = 0$ for $n \neq j$, so $\langle n0|n1\rangle = 0$ and we get

$$\begin{aligned}
(7) \quad E_{n2} &= \langle n0 | V | n1 \rangle \\
(8) \quad &= \sum_{j \neq n} \frac{\langle j0 | V | n0 \rangle \langle n0 | V | j0 \rangle}{E_{n0} - E_{j0}} \\
(9) \quad &= \sum_{j \neq n} \frac{|\langle j0 | V | n0 \rangle|^2}{E_{n0} - E_{j0}}
\end{aligned}$$

As an example, we can revisit the delta function bump in the infinite square well that we considered with first order perturbation theory. In this case

$$(10) \quad |n0\rangle = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

$$(11) \quad E_{n0} = \frac{(n\pi\hbar)^2}{2ma^2}$$

and the perturbation is

$$(12) \quad V = \alpha \delta\left(x - \frac{a}{2}\right)$$

so

$$(13) \quad \langle j0 | V | n0 \rangle = \frac{2\alpha}{a} \sin \frac{j\pi}{2} \sin \frac{n\pi}{2}$$

We then get

$$(14) \quad E_{n2} = \sum_{j \neq n} \frac{|\langle j0 | V | n0 \rangle|^2}{E_{n0} - E_{j0}}$$

$$(15) \quad = \frac{2ma^2}{\pi^2\hbar^2} \frac{4\alpha^2}{a^2} \sin^2 \frac{n\pi}{2} \sum_{j \neq n} \frac{1}{n^2 - j^2} \sin^2 \frac{j\pi}{2}$$

This comes out to

$$(16) \quad E_{n2} = \begin{cases} 0 & n \text{ even} \\ \frac{8m\alpha^2}{\pi^2\hbar^2} \sum_{\text{odd } j \neq n} \frac{1}{n^2 - j^2} & n \text{ odd} \end{cases}$$

The series can be summed exactly, but it's a bit tricky. First, split it into partial fractions:

$$(17) \quad \sum_{\text{odd } j \neq n} \frac{1}{n^2 - j^2} = \frac{1}{2n} \sum_{\text{odd } j \neq n} \left[\frac{1}{n+j} + \frac{1}{n-j} \right]$$

Each term in the $\frac{1}{n+j}$ series cancels with a term in the other series of form $1/(n - (j + 2n)) = -\frac{1}{n+j}$. However, the term $1/(n - 3n)$ doesn't cancel with any term from the $\frac{1}{n+j}$ series since this would require $j = n$, which is excluded from the series. Thus there is a left over term of $1/(n - 3n) = -\frac{1}{2n}$ from the $\frac{1}{n-j}$ series.

The early terms in the $\frac{1}{n-j}$ series do not cancel with terms from the $\frac{1}{n+j}$ series, but they cancel with each other. If $n > j$, $\frac{1}{n-j}$ cancels with $1/(n - (j + 2n - 2j)) = \frac{1}{j-n}$. For a given n , there are $(n-1)/2$ odd integers less than n , so the $\frac{1}{n-j}$ series contains $(n-1)/2$ positive terms which must cancel with other terms from the same series, so the first $n-1$ terms in the $\frac{1}{n-j}$ series cancel each other; beyond that, the terms from the two series cancel each other as shown above, except for the one left over term of $-\frac{1}{2n}$. Therefore, the second order energy correction is

$$(18) \quad E_{n2} = \frac{8m\alpha^2}{\pi^2\hbar^2} \frac{1}{2n} \left(-\frac{1}{2n} \right) = -\frac{2m\alpha^2}{n^2\pi^2\hbar^2}$$

As a second example, we'll look at the second order correction for the perturbed harmonic oscillator. Here, the perturbed potential is

$$(19) \quad V = \frac{1}{2}\epsilon kx^2 = \frac{1}{2}\epsilon m\omega^2 x^2$$

We need the matrix elements $\langle j0|V|n0\rangle$ which we worked out using the raising and lowering operators for the harmonic oscillator. Combining the results from that post, we have

$$(20) \quad X_{nj}^2 = \frac{\hbar}{2m\omega} \left[(2n+1)\delta_{nj} + \sqrt{n(n-1)}\delta_{j,n-2} + \sqrt{(n+1)(n+2)}\delta_{j,n+2} \right]$$

Therefore, for a fixed n , there are only two non-zero terms in the sum for E_{n2} : $j = n-2$ and $j = n+2$. Combining this with $E_{n0} = \hbar\omega(n + \frac{1}{2})$ we have

$$(21) \quad E_{n2} = \left(\frac{\hbar\omega\varepsilon}{4} \right)^2 \left[\frac{(n+1)(n+2)}{-2\hbar\omega} + \frac{n(n-1)}{2\hbar\omega} \right]$$

$$(22) \quad = - \left(n + \frac{1}{2} \right) \hbar\omega \frac{\varepsilon^2}{8}$$

This matches the second order term we found in the expansion of the exact energy in the previous post.

PINGBACKS

Pingback: Harmonic oscillator in an electric field

Pingback: Degenerate perturbation theory: two states

Pingback: Degenerate perturbation in 3 state system

Pingback: Van der Waals interaction

Pingback: Perturbing the wave function (Stark effect and proton electric dipole moment)

Pingback: Variational principle with a two-state hamiltonian