

## SECOND ORDER NON-DEGENERATE PERTURBATION THEORY

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

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

This gives us

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

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

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

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

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

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

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

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

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

$$E_{n2} = \langle n0 | V | n1 \rangle \quad (7)$$

$$= \sum_{j \neq n} \frac{\langle j0 | V | n0 \rangle \langle n0 | V | j0 \rangle}{E_{n0} - E_{j0}} \quad (8)$$

$$= \sum_{j \neq n} \frac{|\langle j0 | V | n0 \rangle|^2}{E_{n0} - E_{j0}} \quad (9)$$

**Example 1.** We revisit the delta function bump in the infinite square well that we considered with first order perturbation theory. In this case

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

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

and the perturbation is

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

so

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

We then get

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

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

This comes out to

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

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

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

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

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

**Example 2.** We look at the second order correction for the perturbed harmonic oscillator. Here, the perturbed potential is

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

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

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

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

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

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

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

## PINGBACKS

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