SECOND ORDER NON-DEGENERATE PERTURBATION THEORY

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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:

$$(H_0+\lambda V)\left(\psi_{n0}+\lambda\psi_{n1}+\lambda^2\psi_{n2}+\ldots\right)=\left(E_{n0}+\lambda E_{n1}+\lambda^2E_{n2}+\ldots\right)\left(\psi_{n0}+\lambda\psi_{n1}+\lambda^2\psi_{n2}+\ldots\right) \tag{1}$$

This gives us

$$H_0\psi_{n2}+V\psi_{n1} = E_{n0}\psi_{n2}+E_{n1}\psi_{n1}+E_{n2}\psi_{n0} \tag{2}$$

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

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

Since H_0 is hermitian, we can swap it to the bra end in the first term and then use $\langle H_0n0|=E_{n0}$, 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

$$E_{n0}\langle n0|n2\rangle+\langle n0|V|n1\rangle=E_{n0}\langle n0|n2\rangle+E_{n1}\langle n0|n1\rangle+E_{n2} \tag{4}$$

$$\langle n0|V|n1\rangle=E_{n1}\langle n0|n1\rangle+E_{n2} \tag{5}$$

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

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

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

$$E_{n2} = \langle n0|V|n1\rangle \tag{7}$$
$$= \sum_{j\neq n} \frac{\langle j0|V|n0\rangle\langle n0|V|j0\rangle}{E_{n0}-E_{j0}} \tag{8}$$
$$= \sum_{j\neq n} \frac{|\langle j0|V|n0\rangle|^2}{E_{n0}-E_{j0}} \tag{9}$$

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

$$|n0\rangle = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \tag{10}$$
$$E_{n0} = \frac{(n\pi\hbar)^2}{2ma^2} \tag{11}$$

and the perturbation is

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

so

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

We then get

$$E_{n2} = \sum_{j\neq n} \frac{|\langle j0|V|n0\rangle|^2}{E_{n0}-E_{j0}} \tag{14}$$
$$= \frac{2ma^2}{\pi^2\hbar^2}\frac{4\alpha^2}{a^2}\sin^2\frac{n\pi}{2}\sum_{j\neq n}\frac{1}{n^2-j^2}\sin^2\frac{j\pi}{2} \tag{15}$$

This comes out to

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

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

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

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

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

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

$$V=\frac{1}{2}\varepsilon kx^2=\frac{1}{2}\varepsilon m\omega^2x^2 \tag{19}$$

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

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

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 $E_{n0}=\hbar\omega\left(n+\frac{1}{2}\right)$ we have

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

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

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

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