Notes on Hydrogenic Perturbation Theory

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November 29, 2017

Summary of Perturbation Theory

In perturbation theory, we want to solve the eigenvalue problem

$$\hat{H}|\psi\rangle = E|\psi\rangle, \tag{1}$$

where $\hat{H} = \hat{H}_0 + \lambda\hat{H}_1$ and we can solve the eigenvalue problem

$$\hat{H}_0|\psi\rangle = E^{(0)}|\psi\rangle. \tag{2}$$

The extra term, $\lambda\hat{H}_1$, is a small correction to $\hat{H}_0$.

Nondegenerate Perturbation Theory

In the case that there is only one eigenstate $|\psi_n^{(0)}\rangle$ in Equation (2) corresponding to energy $E_n^{(0)}$, we seek solutions in the form

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \ldots, \tag{3}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots. \tag{4}$$

We have found the first and second order energy corrections as

$$E_n^{(1)} = \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle, \tag{5}$$

$$E_n^{(2)} = \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(1)}\rangle, \tag{6}$$

where

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}|\psi_n^{(0)}\rangle. \tag{7}$$

This gives,

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left|\langle\psi_m^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}.$$

Degenerate Perturbation Theory

In the case that there are several eigenstates $|\psi_{n,i}^{(0)}\rangle$, $i = 1, \ldots. N$, in Equation (2) corresponding to energy $E_n^{(0)}$, we seek solutions in the form

$$|\psi_n\rangle = \sum_{i=1}^{N} c_i|\psi_{i,n}^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \ldots, \tag{8}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \ldots. \tag{9}$$

The goal is to find the c_i's so that linear combinations the zeroth order solution correspond to first order energy shifts which are the eigenvalues of the eigenvalue problem

$$H_1 \mathbf{c} = E_n^{(1)} \mathbf{c}, \tag{10}$$

where

$$(H_1)_{ji} = \langle \psi_{n,j}^{(0)} | \hat{H}_1 | \psi_{n,i}^{(0)} \rangle.$$

Since there can be several solutions of this eigenvalue problem, there will be several linear combinations the zeroth order solution.

Example 1. Stark Effect

$$\hat{H} = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{|\hat{\mathbf{r}}|} + e\hat{\mathbf{r}} \cdot \mathbf{E}$$

Picking $\mathbf{E} = E\mathbf{k}$, then $\hat{H}_1 = e|\mathbf{E}|\hat{z}$. The ground state, $|1,0,0\rangle$, in nondegenerate. The first order correction is $E_n^{(1)} = e|\mathbf{E}|\langle 1,0,0|\hat{z}|1,0,0\rangle = 0$. It vanishes due to parity considerations.One needs higher order corrections to get nonzero contributions.

The first excites states, for $n = 2$, are degenerate. There are $n^2 = 4$ states: $|2,0,0\rangle$, $|2,1,0\rangle$, $|2,1,1\rangle$, and $|2,1,-1\rangle$. The only nonzero matrix entries are

$$(H_1)_{ji} = \langle \psi_{n,j}^{(0)} | \hat{H}_1 | \psi_{n,i}^{(0)} \rangle.$$

For example,

$$\langle 200|\hat{H}_1|210\rangle = e|\mathbf{E}| \int_0^\infty r^2\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi R_{20}^* Y_{00}^* r\cos\theta R_{21} Y_{10}.$$

This gives

$$\langle 200|\hat{H}_1|210\rangle = -3e|\mathbf{E}|a_0.$$

These computations give

$$H = \begin{pmatrix} 0 & -\beta & 0 & 0 \\ -\beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{11}$$

where $\beta = 3e|\mathbf{E}|a_0$.

We can use this matrix representation to solve the eigenvalue problem

$$\begin{pmatrix} 0 & -\beta & 0 & 0 \\ -\beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E_2^{(1)} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \tag{12}$$

We obtain the possible first order corrections to the energy from the eigenvalue equation:

$$\begin{vmatrix} -E_2^{(1)} & -\beta & 0 & 0 \\ -\beta & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = \left(-E_2^{(1)}\right)^2 \left[\left(E_2^{(1)}\right)^2 - \beta^2\right] = 0.$$

Therefore,

$$-E_2^{(1)} = 0, 0, \beta, -\beta.$$

The corresponding normalized eigenvectors associated with these eigenvalues are given respectively by

$$|2,0,1\rangle, |2,0,-1\rangle, \frac{1}{\sqrt{2}}\left(|2,1,0\rangle - |2,0,0\rangle\right), \frac{1}{\sqrt{2}}\left(|2,1,0\rangle + |2,0,0\rangle\right).$$

Only the last two states give a shift to first order in the energies.

Hydrogen Atom Perturbations

Recall that the zeroth order energies are given by

$$E_n^{(0)} = -\frac{\mu c^2 Z^2 \alpha^2}{2n^2}.$$

There are relativistic corrections of order α^4, where $\alpha = \frac{1}{137}$. These are the correction to the kinetic energy, spin-orbit coupling, and the Darwin term. These perturbations to the Hamiltonian are given by

$$\hat{H}_K = -\frac{\hat{p}^4}{8m_e^3c^2}, \tag{13}$$

$$\hat{H}_{SO} = \frac{Ze^2}{2m_e^2c^2|\hat{r}|^3}\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \tag{14}$$

$$\hat{H}_D = -\frac{1}{8m_e^2c^2}[\hat{\mathbf{p}}, [\hat{\mathbf{p}}, V(\hat{\mathbf{r}})]]. \tag{15}$$

A little effort is needed to apply perturbation theory to these corrections to obtain the corrections to the energies. The relativistic correction to the kinetic energy has rotational invariance, so the degenerate eigenspaces result in diagonal matrix representations for H_1. One only needs to compute

$$E_{n,\ell}^{(1)} = \langle n,\ell,m|\hat{H}_K|n,\ell,m\rangle = -\frac{1}{2}m_e c^2 Z^4 \alpha^4 \left[-\frac{3}{4n^4} + \frac{1}{n^3\left(\ell + \frac{1}{2}\right)}\right]. \tag{16}$$

For the spin-orbit term, one needs basis states coupling position and spin states, $|\ell, m, \pm\mathbf{z}\rangle$. $\hat{H}_{SO}$ commutes with $\hat{J}_z$ and $\hat{\mathbf{J}}^2$. Eigenvalues of $\hat{J}_z$ equal to $m + \frac{1}{2}$ correspond to the two states $|\ell, m, +\mathbf{z}\rangle$ and $|\ell, m+1, -\mathbf{z}\rangle$ for fixed ℓ and $m \neq \ell$.

Noting that

$$2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+ + 2\hat{L}_z\hat{S}_z,$$

the matrix representation for $2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ is

$$\hbar^2 \begin{pmatrix} m & \sqrt{\ell(\ell+1) - m(m+1)} \\ \sqrt{\ell(\ell+1) - m(m+1)} & -(m+1) \end{pmatrix}. \tag{17}$$

Solving the eigenvalue problem,

$$2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}|\lambda\rangle = \lambda\hbar^2|\lambda\rangle,$$

one finds the eigenvalues $\lambda = \ell, -(\ell+1)$ and the corresponding states

$$\begin{aligned} |j = \ell \pm \frac{1}{2}, m_j\rangle &= \sqrt{\frac{\ell \pm m_j + \frac{1}{2}}{2\ell+1}}|\ell, m_j - \frac{1}{2}, +\mathbf{z}\rangle \\ &\pm\sqrt{\frac{\ell \mp m_j + \frac{1}{2}}{2\ell+1}}|\ell, m_j + \frac{1}{2}, +\mathbf{z}\rangle. \end{aligned} \tag{18}$$

Eventually, this leads to the result

$$E_{SO}^{(1)} = \frac{m_e c^2 Z^4 \alpha^4}{4n^3 \ell(\ell + \frac{1}{2})(\ell+1)} \begin{cases} \ell, & j = \ell + \frac{1}{2}, \\ -(\ell+1), & j = \ell - \frac{1}{2}. \end{cases} \tag{19}$$

There is still the Darwin term. The final result for the total energy shifts

$$E_{n,j}^{(1)} = -\frac{m_e c^2 (Z\alpha)^4}{2n^3} \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right). \tag{20}$$