Lecture 8: Time-independent Perturbation Theory

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We can use the perturbation theory to solve a system that is "close" to another system that has an exact solution. For example, if $\mathcal{H}$ is close to $\mathcal{H}_0$ and we know eigenvalues and the corresponding eigenstates for $\mathcal{H}_0$, then we can use perturbation theory to approximate eigenenergies and eigenstates of $\mathcal{H}$.

Suppose that the system is described by

$$\mathcal{H} = \mathcal{H}_0 + \lambda V,$$

then we can solve the eigenvalue problem

$$\mathcal{H} \left| \psi \right\rangle = E \left| \psi \right\rangle$$

as a power series of λ, where we can write both the eigenenergies and eigenstates in a power series of λ. We note that as $\lambda \to 0$, $\mathcal{H} \to \mathcal{H}_0$ and we recover the exact solution. Therefore, perturbation theory works well if $\lambda \ll 1$.

For this lecture, we will consider the time-independent perturbation theory using the Rayleigh-Schrödinger formulation. We will first discuss the non-degenerate case and later will consider the degenerate separately.

8.1   Non-degenerate time-independent perturbation theory

As stated earlier, the Hamiltonian is described by

$$\mathcal{H} = \mathcal{H}_0 + \lambda V,$$

where H is time-independent. $\mathcal{H}_0$ can be solved exactly for the eigenstates $\left| n^{(0)} \right\rangle$ and the corresponding eigenenergies E_n. That is,

$$\mathcal{H}_0 \left| n^{(0)} \right\rangle = E_n^{(0)} \left| n^{(0)} \right\rangle, \quad \left\langle n^{(0)} \middle| m^{(0)} \right\rangle = \delta_{nm}.$$

For the whole system of the Hamiltonian $\mathcal{H}$, we have

$$\mathcal{H} \left| n \right\rangle = E_n \left| n \right\rangle,$$

where $\left| n \right\rangle$ and E_n can be solved perturbatively in a power series of λ. For convenience, we choose

$$\left\langle n^{(0)} \middle| n \right\rangle = 1,$$

which does not mean that $\left| n^{(0)} \right\rangle = \left| n \right\rangle$ but implies that $\left| n \right\rangle$ can have a component perpendicular to $\left| n^{(0)} \right\rangle$. We also assume that $E_n^{(0)}$ are non-degenerate, *i.e.* $E_n^{(0)} \neq E_m^{(0)}$ if $n \neq m$.

In order to solve $\mathcal{H}$, we expand $\left| n \right\rangle$ and E_n in a power series of λ,

$$
\begin{aligned}
\left| n \right\rangle &= \left| n^{(0)} \right\rangle + \lambda \left| n^{(1)} \right\rangle + \lambda^2 \left| n^{(2)} \right\rangle + \cdots \\
E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots.
\end{aligned}
$$

We choose the normalization condition such that

$$\langle n^{(0)} | n \rangle = 1, \quad \forall \lambda$$

$$\Rightarrow \quad \langle n^{(0)} | n^{(k)} \rangle = 0, \quad \forall k > 0.$$

The second condition implies that higher-order terms are "perpendicular" to the unperturbed state $|n^{(0)}\rangle$. When substituting $|n\rangle$ and E_n into the Schrödinger equation, we have

$$(\mathcal{H}_0 + \lambda V) \left(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots \right) = \left(E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots \right) \left(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots \right).$$

We then group terms with the same order of λ:

$$\lambda^0 \quad : \quad \mathcal{H}_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

$$\lambda^1 \quad : \quad \mathcal{H}_0 |n^{(1)}\rangle + V |^{(0)}\rangle = E_n^{(0)} |n^{(1)}\rangle + E_n^{(1)} |n^{(0)}\rangle$$

$$\vdots$$

$$\lambda^k \quad : \quad \mathcal{H}_0 |n^{(k)}\rangle + V |^{(k-1)}\rangle = E_n^{(0)} |n^{(k)}\rangle + E_n^{(1)} |n^{(k-1)}\rangle + \cdots + E_n^{(k)} |n^{(0)}\rangle$$

Note that we want to solve for $|n^{(k)}\rangle$ and $E_n^{(k)}$, $\forall k$. First in order to solve for $E_n^{(k)}$, we will take an inner product of the last equation with $\langle n^{(0)} |$:

$$\langle n^{(0)} | \mathcal{H}_0 | n^{(k)} \rangle + \langle n^{(0)} | V | n^{(k-1)} \rangle = E_n^{(k)} \quad \text{since } \langle n^{(0)} | n^{(k)} \rangle = \delta_{k,0},$$

but $\langle n^{(0)} | \mathcal{H}_0 | n^{(k)} \rangle = E_n^{(0)} \langle n^{(0)} | n^{(k)} \rangle = 0.$

$$\Rightarrow \quad \boxed{E_n^{(k)} = \langle n^{(0)} | V | n^{(k-1)} \rangle}.$$

Now in order to find $|n^{(k)}\rangle$, we take an inner product with $\langle m^{(0)} |$, where $m \neq n$:

$$\langle m^{(0)} | E_n^{(0)} - \mathcal{H}_0 | n^{(k)} \rangle = \langle m^{(0)} | \left[\left(V - E_n^{(1)} \right) |n^{(k-1)}\rangle - E_n^{(2)} |n^{(k-2)}\rangle - \cdots - E_n^{(k-1)} |n^{(1)}\rangle \right]$$

$$\left(E_n^{(0)} - E_m^{(0)} \right) \langle m^{(0)} | n^{(k)} \rangle = \langle m^{(0)} | \left[\left(V - E_n^{(1)} \right) |n^{(k-1)}\rangle - E_n^{(2)} |n^{(k-2)}\rangle - \cdots - E_n^{(k-1)} |n^{(1)}\rangle \right]$$

$$\Rightarrow \quad \langle m^{(0)} | n^{(k)} \rangle = \frac{1}{E_n^{(0)} - E_m^{(0)}} \langle m^{(0)} | \left[\left(V - E_n^{(1)} \right) |n^{(k-1)}\rangle - E_n^{(2)} |n^{(k-2)}\rangle - \cdots - E_n^{(k-1)} |n^{(1)}\rangle \right]$$

We apply an operator

$$Q_n \equiv \mathbb{1} - |n^{(0)}\rangle \langle n^{(0)}| = \sum_{m \neq n} |m^{(0)}\rangle \langle m^{(0)}|$$

to both sides of the above equation. We note that Q_n is a projection operator that projects onto a subspace that is orthogonal to $|n^{(0)}\rangle$. We have

$$\sum_{m \neq n} |m^{(0)}\rangle \langle m^{(0)} | n^{(k)} \rangle = \sum_{m \neq n} \frac{|m^{(0)}\rangle \langle m^{(0)}|}{E_n^{(0)} - E_m^{(0)}} \left[\left(V - E_n^{(1)} \right) |n^{(k-1)}\rangle - E_n^{(2)} |n^{(k-2)}\rangle - \cdots - E_n^{(k-1)} |n^{(1)}\rangle \right],$$

but

$$\sum_{m \neq n} |m^{(0)}\rangle \langle m^{(0)} | n^{(k)} \rangle = \sum_{\text{all } m} |m^{(0)}\rangle \langle m^{(0)} | n^{(k)} \rangle - \langle n^{(0)} | n^{(k)} \rangle = \sum_{\text{all } m} |m^{(0)}\rangle \langle m^{(0)} | n^{(k)} \rangle = |n^{(k)}\rangle,$$

since $\langle n^{(0)} \mid n^{(k)} \rangle = 0$ and $\sum_{\text{all } m} \left| m^{(0)} \right\rangle \left\langle m^{(0)} \right| = 1$. Therefore, we have

$$\left| n^{(k)} \right\rangle = \sum_{m \neq n} \frac{\left| m^{(0)} \right\rangle \left\langle m^{(0)} \right|}{E_n^{(0)} - E_m^{(0)}} \left[\left(V - E_n^{(1)} \right) \left| n^{(k-1)} \right\rangle - E_n^{(2)} \left| n^{(k-2)} \right\rangle - \cdots - E_n^{(k-1)} \left| n^{(1)} \right\rangle \right],$$

or

$$\left| n^{(k)} \right\rangle = \frac{Q_n}{E_n^{(0)} - \mathcal{H}_0} \left[\left(V - E_n^{(1)} \right) \left| n^{(k-1)} \right\rangle - E_n^{(2)} \left| n^{(k-2)} \right\rangle - \cdots - E_n^{(k-1)} \left| n^{(1)} \right\rangle \right],$$

where

$$\frac{Q_n}{E_n^{(0)} - \mathcal{H}_0} = \sum_{m \neq n} \frac{\left| m^{(0)} \right\rangle \left\langle m^{(0)} \right|}{E_n^{(0)} - E_m^{(0)}}.$$

We can use the above equations for $E_n^{(k)}$ and $\left| n^{(k)} \right\rangle$ to calculate any order k^{th} term in the perturbation. However, we note that in order to calculate $E_n^{(k)}$ and $\left| n^{(k)} \right\rangle$ we have to fist know $E_n^{(l)}$ and $\left| n^{(l)} \right\rangle$, $\forall l < k$. Therefore, we have to start from the lowest order term and work our way up to the kth order.

As an example, we will only consider low level calculations.

- $E_n^{(1)}$: first-order correction of eigenenergies

$$E_n^{(1)} = \left\langle n^{(0)} \left| V \right| n^{(0)} \right\rangle,$$

  and so,

$$E_n = E_n^{(0)} + \lambda \left\langle n^{(0)} \left| V \right| n^{(0)} \right\rangle + \mathcal{O}\left(\lambda^2 \right)$$

- $\left| n^{(1)} \right\rangle$: first-order correction of eigenstates

$$\left| n^{(1)} \right\rangle = \sum_{m \neq n} \frac{\left| m^{(0)} \right\rangle \left\langle m^{(0)} \right|}{E_n^{(0)} - E_m^{(0)}} \left(V - E_n^{(1)} \right) \left| n^{(0)} \right\rangle = \sum_{m \neq n} \frac{\left| m^{(0)} \right\rangle \left\langle m^{(0)} \left| V \right| n^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}},$$

  since $\left\langle m^{(0)} \left| E_n^{(1)} \right| n^{(0)} \right\rangle = \delta_{m,n} = 0$ for $m \neq n$. We let $V_{mn} = \left\langle m^{(0)} \left| V \right| n^{(0)} \right\rangle$.

$$\Rightarrow \quad \left| n^{(1)} \right\rangle = \sum_{m \neq n} \left| m^{(0)} \right\rangle \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}},$$

  and

$$\Rightarrow \quad |n\rangle = \left| n^{(0)} \right\rangle + \lambda \left| n^{(1)} \right\rangle + \mathcal{O}\left(\lambda^2 \right) \left| n^{(k)} \right\rangle.$$

- $E_n^{(2)}$: second-order correction of eigenenergies

$$E_n^{(2)} = \left\langle n^{(0)} \left| V \right| n^{(1)} \right\rangle$$

$$= \left\langle n^{(0)} \left| V \left(\sum_{m \neq n} \left| m^{(0)} \right\rangle \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \right) \right.$$

$$\Rightarrow \quad E_n^{(2)} = \sum_{m \neq n} \frac{\left| \left\langle m^{(0)} \left| V \right| n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} = \sum_{m \neq n} \frac{V_{nm} V_{mn}}{E_n^{(0)} - E_m^{(0)}}$$

  We can continue this process for higher order but we will stop only the second-order correction of eigenenergies. We note that for the second-order correction,

1. the second-order correction to the ground state $E_0^{(2)}$ is always negative since $E_0^{(0)} < E_{m \neq 0}^{(0)}$, and hence the denominator is always negative.

2. two levels that are coupled to each other such that $V_{mn} \neq 0$ rebels each other. That is, if $E_n^{(0)}$ and $E_m^{(0)}$ are close ($E_m^{(0)} - E_n^{(0)} \sim \epsilon$) and $E_n^{(0)} < E_m^{(0)}$, then

$$\Rightarrow \quad E_n^{(2)} = -\frac{|V_{mn}|^2}{\epsilon} \quad \text{and} \quad E_m^{(2)} = \frac{|V_{mn}|^2}{\epsilon}.$$

That is, the state $\left|n^{(0)}\right\rangle$ is pushed downward while $\left|m^{(0)}\right\rangle$ is pushed upward in energy. More generally, there can be no level-crossing if the two states are coupled through the perturbed potential.

We will next discuss a general structure of the perturbation expansion. For brevity, we will use the following abbreviation

$$|0\rangle \equiv \left|n^{(0)}\right\rangle, \quad |k\rangle \equiv \left|n^{(k)}\right\rangle, \quad \text{and } \Delta \equiv E_n^{(0)} - H_0.$$

The kth−order correction of eigenenergies and eigenstates can be rewritten as

$$
\begin{aligned}
E^{(k)} &= \langle 0|V|k-1\rangle \\
|k\rangle &= \frac{Q}{\Delta}\left[\left(V - E^{(1)}\right)|k-1\rangle - E^{(2)}|k-2\rangle - \cdots - E^{(k-1)}|1\rangle\right].
\end{aligned}
$$

Some of the low-level corrections can be written as

$$
\begin{aligned}
E^{(1)} &= \langle 0|V|0\rangle \equiv \langle V\rangle \\
|1\rangle &= \frac{Q}{\Delta}V|0\rangle \\
E^{(2)} &= \langle 0|V|1\rangle = \left\langle 0\left|V\frac{Q}{\Delta}V\right|0\right\rangle \equiv \left\langle V\frac{Q}{\Delta}V\right\rangle \\
|2\rangle &= \frac{Q}{\Delta}\left(V - E^{(1)}\right)|1\rangle = \frac{Q}{V}\left(V - \langle V\rangle\right)\frac{Q}{\Delta}V|0\rangle \\
E^{(3)} &= \langle 0|V|2\rangle = \left\langle 0\left|V\frac{Q}{\Delta}\left(V - \langle V\rangle\right)\frac{Q}{\Delta}V\right|0\right\rangle \equiv \left\langle V\frac{Q}{\Delta}\left(V - \langle V\rangle\right)\frac{Q}{\Delta}V\right\rangle \\
|3\rangle &= \frac{Q}{\Delta}\left(V - E^{(1)}\right)|2\rangle - E^{(2)}|1\rangle = \frac{Q}{\Delta}\left[\left(V - \langle V\rangle\right)\frac{Q}{\Delta}\left(V - \langle V\rangle\right) - \left\langle V\frac{Q}{\Delta}V\right\rangle\right]\frac{Q}{\Delta}V|0\rangle \\
&\vdots
\end{aligned}
$$

A few notes about the perturbation expansion:

- The expansion is systematic but it becomes long and complicated very quickly.

- The recursion relation is easy to automate.

- Alternative approaches such as the Brillouin-Wigner method have a similar structure but the equations for E_n are non-linear; however we do not have to consider non-degenerate and degenerate cases separately.

8.2 Wavefunction normalization

Normally, an eigenstate obtained from the perturbation calculation is not normalized. In this section, we will attempt to interpret the correction to the eigenstate. We define the normalized eigenstate as

$$|n\rangle_N = \mathcal{Z}_n^{1/2} |n\rangle \quad \text{and} \quad {}_N\langle n|n\rangle_N = 1,$$

where $\mathcal{Z}$ is a normalization factor and $|n\rangle$ is an eigenstate obtained from the perturbation calculation.

$$
\begin{aligned}
\mathcal{Z}_n &= \frac{1}{\langle n|n\rangle} \\
\Rightarrow \quad \mathcal{Z}^{-1} &= \langle n|n\rangle = 1 + \lambda^2 \langle n^{(1)}|n^{(1)}\rangle + \cdots \\
&= 1 + \lambda^2 \sum_{m \neq n} \frac{V_{nm}V_{mn}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} + \cdots.
\end{aligned}
$$

For small λ, we have

$$\Rightarrow \quad \mathcal{Z}_n \sim 1 - \lambda^2 \sum_{m \neq n} \frac{V_{nm}V_{mn}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} + \cdots,$$

where the second term on the right hand side represents the probability for the "leakage" into other states of order λ^2. We note that

$$
\begin{aligned}
\left\langle n^{(0)} \middle| n \right\rangle_N &= \mathcal{Z}_n^{1/2} \left\langle n^{(0)} \middle| n \right\rangle \quad \text{but} \quad \left\langle n^{(0)} \middle| n \right\rangle = 1 \\
\Rightarrow \quad \mathcal{Z}_n^{1/2} &= \left\langle n^{(0)} \middle| n \right\rangle_N \\
\Rightarrow \quad \mathcal{Z}_n &= \left| \left\langle n^{(0)} \middle| n \right\rangle_N \right|^2.
\end{aligned}
$$

Therefore, $\mathcal{Z}_N$ denotes the probability of finding the perturbed eigenstate $|n\rangle$ in the original eigenstate $\left|n^{(0)}\right\rangle$, which is always less than an identity since there is a "leakage" of the probability to other states $\left|m^{(0)}\right\rangle$, where $m \neq n$, as previously shown.

8.3 Applications of Perturbation Theory

In this section, we will discuss how we can use the perturbation theory to calculate or approximate eigenenergies and eigenstates of a quantum mechanical system.

8.3.1 Anharmonic oscillator

Consider an anhormonic oscillator described by the following Hamiltonian

$$\mathcal{H} = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2 + \lambda m\omega^2 X.$$

This problem can be solved exactly by rewriting the Hamiltonian as

$$\mathcal{H} = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 \left(X + \lambda\right)^2 - \frac{1}{2}m\omega^2\lambda^2,$$

and hence the eigenenergies for this system are

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{1}{2}m\omega^2\lambda^2$$

We will compare this result with one obtained from the perturbation calculation. The perturbed potential is given by

$$\lambda V = \lambda m\omega^2 X,$$

where $\lambda \ll 1$ and $X = \sqrt{\dfrac{\hbar}{2m\omega}}\left(a + a^\dagger\right)$. The first-order correction of E_n is

$$E_n^{(n)} = \left\langle n^{(0)} \left| m\omega^2 X \right| n^{(0)} \right\rangle = m\omega^2 \sqrt{\frac{\hbar}{2m\omega}} \left\langle n^{(0)} \left| \left(a + a^\dagger\right) \right| n^{(0)} \right\rangle = 0.$$

Since the first-order correction vanishes, we will consider the second order correction of E_n,

$$
\begin{aligned}
E_n^{(2)} &= \sum_{m \neq n} \frac{\left\langle n^{(0)} \left| m\omega^2 X \right| m^{(0)} \right\rangle \left\langle m^{(0)} \left| m\omega^2 X \right| n^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \\
\Rightarrow \quad E_n^{(2)} &= m^2\omega^4 \frac{\hbar}{2m\omega}\frac{1}{\hbar\omega}\left(-(n+1) + n\right) \\
\Rightarrow \quad E_n^{(2)} &= -\frac{1}{2}m\omega^2
\end{aligned}
$$

Therefore, up to second order, we have

$$E_n = E_n^{(0)} + \lambda E_n(1) + \lambda^2 E_n^{(2)} + \cdots = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{1}{2}m\omega^2\lambda^2,$$

which is exactly equal to the exact solution. The first-order correction of the eigenstate $|n\rangle$ can be calculated using

$$\left| n^{(1)} \right\rangle = \sum_{m \neq n} \left| m^{(0)} \right\rangle \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}},$$

where

$$
\begin{aligned}
V_{mn} &= \left\langle m^{(0)} \left| m\omega^2 X \right| n^{(0)} \right\rangle \\
&= m\omega^2 \sqrt{\frac{\hbar}{2m\omega}} \left\langle m^{(0)} \left| \left(a + a^\dagger\right) \right| n^{(0)} \right\rangle \\
&= m\omega^2 \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n}\,\delta_{m,n-1} + \sqrt{n+1}\,\delta_{m,n+1}\right).
\end{aligned}
$$

We then have

$$
\begin{aligned}
\Rightarrow \quad \left| n^{(1)} \right\rangle &= m\omega^2 \sqrt{\frac{\hbar}{2m\omega}}\frac{1}{m\omega}\left(\sqrt{n}\left|(n-1)^{(0)}\right\rangle - \sqrt{n+1}\left|(n+1)^{(0)}\right\rangle\right) \\
&= \sqrt{\frac{m\omega}{2\hbar}}\left(\sqrt{n}\left|(n-1)^{(0)}\right\rangle - \sqrt{n+1}\left|(n+1)^{(0)}\right\rangle\right) \\
\Rightarrow \quad |n\rangle &= \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle = \left|n^{(0)}\right\rangle + \lambda\sqrt{\frac{m\omega}{2\hbar}}\left(\sqrt{n}\left|(n-1)^{(0)}\right\rangle - \sqrt{n+1}\left|(n+1)^{(0)}\right\rangle\right)
\end{aligned}
$$

Using $\left| n^{(1)} \right\rangle$, we can calculate the second-order correction of eigenergies $E_n^{(2)}$ as

$$
\begin{aligned}
E_N^{(2)} &= \left\langle n^{(0)} \left| V \right| n^{(1)} \right\rangle \\
&= \sqrt{\frac{m\omega}{2\hbar}} m\omega^2 \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n} \left\langle n^{(0)} \left| \left(a + a^\dagger\right) \right| (n-1)^{(0)} \right\rangle - \sqrt{n-1} \left\langle n^{(0)} \left| \left(a + a^\dagger\right) \right| (n+1)^{(0)} \right\rangle \right) \\
&= \frac{1}{2} m\omega^2 \left(n - n - 1 \right) \\
&= -\frac{1}{2} m\omega^2
\end{aligned}
$$

Therefore, we obtain exactly the same solution as before. That is,

$$
E_n = \hbar\omega \left(n + \frac{1}{2} \right) - \frac{1}{2} m\omega^2 \lambda^2.
$$

8.3.2 Real hydrogen atom

In this section, we will discuss the use of the perturbation theory to calculate energy shifts in a real hydrogen atom.

1. **Relativistic correction to energy**

   We will consider the relativistic kinetic energy of an electron in a hydrogen atom, where

   $$
   E = \sqrt{p^2 c^2 + m^2 c^4} = mc^2 \sqrt{1 + \frac{p^2}{m^2 c^2}}.
   $$

   For $\frac{p^2}{m^2 c^2} \ll 1$, we can approximate E using $(1 + x)^n \sim 1 + nx + \frac{n(n-1)}{2!} x^2$ as

   $$
   E \sim mc^2 \left(1 + \frac{1}{2} \frac{p^2}{m^2 c^2} + \frac{1}{2} \left(-\frac{1}{2} \right) \frac{1}{2} \frac{p^2}{m^4 c^4} \right) = mc^2 + \frac{p^2}{2m} - \frac{1}{8} \frac{p^4}{m^3 c^2},
   $$

   where the first term is the rest energy, the second term is the classical kinetic energy, and the last term is the second order correction of the kinetic energy and is normally small for a particle with small velocity. We, therefore, can treat the last term perturbatively, and re-write the perturbed potential V as

   $$
   V = -\frac{1}{8} \frac{p^4}{m^3 c^2} = -\frac{1}{2mc^2} \left(\frac{p^2}{2m} \right)^2.
   $$

The first-order energy correction to the ground state $|n, lm,\rangle = |1, 0, 0\rangle$ of the "ideal" hydrogen is

$$
\begin{aligned}
E_{n=1}^{(1)} &= -\frac{1}{2mc^2} \left\langle 1,0,0 \left| \left(\frac{p^2}{2m}\right)^2 \right| 1,0,0 \right\rangle \\
&= -\frac{1}{2mc^2} \left\langle 1,0,0 \left| \left(H_0 + \frac{e^2}{r}\right)^2 \right| 1,0,0 \right\rangle \\
&= -\frac{1}{2mc^2} \left(E_1^2 + 2E_1 e^2 \left\langle \frac{1}{r} \right\rangle + e^4 \left\langle \frac{1}{r^2} \right\rangle \right) \\
&= -\frac{1}{2mc^2} \left[\left(\frac{e^2}{2a_0}\right)^2 - 2\left(\frac{e^2}{2a_0}\right) e^2 \frac{1}{a_0} + \frac{2e^4}{a_0^2} \right] \\
&= -\frac{1}{2mc^2} \frac{e^4}{a_0^2} \left(\frac{1}{4} - 1 + 2 \right) \\
\Rightarrow \quad E_{n=1}^{(1)} &= -\frac{5}{4} \frac{1}{2mc^2} \frac{e^4}{a_0^2}.
\end{aligned}
$$

We can write $E_{n=1}^{(1)}$ in terms of $\alpha \equiv \frac{e^2}{\hbar c} \approx \frac{1}{137}$ (where $a_0 = \frac{\hbar^2}{me^2}$), as

$$
E_{n=1}^{(1)} = -\frac{5}{8} mc^2 \alpha^4.
$$

For general n, we have

$$
E_n^{(1)} = -\frac{1}{2} mc^2 \alpha^4 \left(\frac{1}{n^3 (l + 1/2)} - \frac{3}{4n^4} \right)
$$

We note that for hydrogen atom,

$$
E_n = -\frac{1}{2n^2} mc^2 \alpha^2 = -\frac{13.6}{n^2} \text{ eV}
$$

Therefore, $E_1^{(1)}$ is approximately lower than E_1 by a factor of $\alpha^2 \sim 5 \times 10^{-5}$. We will see later that this relativistic correction is of the same order of magnitude as the spin-orbit coupling, and hence we normally combine the two effects and collectively call them the *fine structure splitting*, which will be discussed in more detail later.

2. **Non-degenerate Stark effect** ($\vec{E}-$field)

   An hydrogen atom is in an external electric field and the potential term that we will treat perturbatively is described by
   $$
   V(z) = -eEZ,
   $$
   where we suppose that the electric field is along the $z-$axis, that is $\vec{E} = E\hat{z}$. For the non-degenerate ground state $n = 1$, the first order correction to the eigenenergy is

   $$
   E_{n=1}^{(1)} = -eE \langle 1,0,0|Z|1,0,0\rangle = 0,
   $$

   since $|1, 0, 0\rangle$ is even under parity while the operator Z is odd under parity. Therefore, we will have to consider the second-order correction.

   $$
   E_{n=1}^{(2)} = e^2 E^2 \sum_{(n,l,m) \neq (1,0,0)} \frac{\langle 1,0,0|Z|n,l,m\rangle \langle n,l,m|Z|1,0,0\rangle}{E_1^{(0)} - E_n^{(0)}}.
   $$

We note that

$$\frac{2a_0}{e^2} \leqslant \left| \frac{1}{E_1^{(0)} - E_n^{(0)}} \right| \leqslant \frac{4}{3} \frac{2a_0}{e^2},$$

where the term on the left denote the case where $n \to \infty$ and that on the right where $n = 2$. For the numerator, we have

$$
\begin{aligned}
\sum_{(n,l,m) \neq (1,0,0)} |\langle 1,0,0|Z|n,l,m\rangle|^2 &= \sum_{(n,l,m)} |\langle 1,0,0|Z|n,l,m\rangle|^2 - |\langle 1,0,0|Z|1,0,0\rangle|^2 \\
&= \sum_{(n,l,m)} |\langle 1,0,0|Z|n,l,m\rangle|^2, \quad \text{where } \langle 1,0,0|Z|1,0,0\rangle = 0 \\
&= \sum_{(n,l,m)} \langle 1,0,0|Z|n,l,m\rangle \langle n,l,m|Z|1,0,0\rangle = \langle 1,0,0|Z^2|1,0,0\rangle \\
\Rightarrow \sum_{(n,l,m) \neq (1,0,0)} |\langle 1,0,0|Z|n,l,m\rangle|^2 &= a_0^2.
\end{aligned}
$$

Therefore, the second order correction of the ground state is

$$\Rightarrow \quad -\frac{8}{3}a_0^3 E^2 \leqslant E_1^{(2)} \leqslant -2a_0^3 E^2.$$

Exact calculations yield

$$E_1^{(2)} = -\frac{9}{4}a_0^3 E^2.$$

3. **Linear Stark Effect for $n = 2$**

   Since the $n = 2$ states are degenerate, we will first discuss the degenerate perturbation calculations.

   Degenerate Perturbation Theory

   From the non-degenerate perturbation calculations, we derived the correction to the state $|n\rangle$ and obtained

   $$|n\rangle = \left|n^{(0)}\right\rangle + \lambda \sum_{m \neq n} \left|m^{(0)}\right\rangle \frac{\langle m^{(0)} | V | n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} + \mathcal{O}(\lambda^2).$$

   As you can see that there will be a divergent problem if $E_n^{(0)} - E_m^{(0)} = 0$ and $V_{mn} \equiv \langle m^{(0)} | V | n^{(0)}\rangle \neq 0$. We can resolve this issue by requiring that the matrix element $V_{mn} = 0$ as well by choosing a new basis for degenerate states such that the off-diagonal matrix elements of V is also zero. Therefore, the solution is to diagonalize V in the degenerate subspace.

   Let $\mathcal{S}$ be the degenerate subspace. Therefore, $E_l^{(0)}$ is the same $\forall l \in \mathcal{S}$. Now, we can choose a basis $|l\rangle^{(0)}$ so that

   $$\left\langle l^{(0)} \middle| V \middle| k^{(0)} \right\rangle = 0, \quad l, k \in \mathcal{S} \text{ and } l \neq k.$$

   The result is that the off-diagonal elements of V in this basis $\left|l^{(0)}\right\rangle$ are all zero. We note that $\left\langle l^{(0)} \middle| V \middle| n^{(0)} \right\rangle$ can be non-zero for $l \in \mathcal{S}$ but $n \notin \mathcal{S}$.

   Now we are ready to calculate the linear Stark effect for $n = 2$ (note that by "linear", we mean the first-order correction, which is linear in λ).

   For $n = 2$, there are four degenerate states,

 $$|2,1,1\rangle, \quad |2,1,0\rangle, \quad |2,1,-1\rangle, \quad \text{and } |2,0,0\rangle.$$

We construct the V matrix in the degenerate subspace of the $n = 2$ states. We note that $\langle n, l, m|Z|n, l', m'\rangle \neq 0$ only if $m = m'$, since $[J_z, Z] = 0$. That is, the eigenstates of J_z with the same m is also eigenstate of Z. Therefore, the non-zero matrix elements are

$$\langle 2, 0, 0|Z|2, 1, 0\rangle = \langle 2, 0, 0|Z|2, 1, 0\rangle = -3a_0,$$

where in the integral $Z \to r\cos\theta$, and we obtain the matrix for V as

$$V = \begin{pmatrix} 0 & 3a_0 eE & 0 & 0 \\ 3a_0 eE & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

We diagonalize this matrix and obtain the eigenvalues $0, 0, \pm 3a_0 eE$. The splitting of the $n = 2$ energy states due to the external electric field is shown in the diagram below
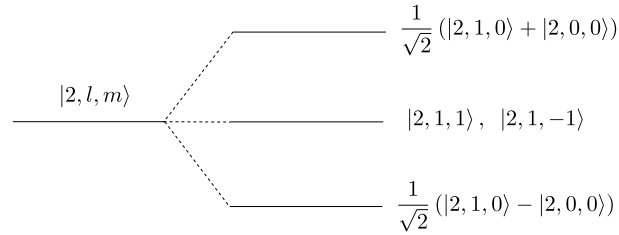
4. **Spin-orbit splitting** (fine structure)

So far we have been ignoring an electron spin in the consideration of the hydrogen atom. When the spin is considered, there are 2 degenerate states for each electronic states corresponding to spin-up and spin-down. This spin state can interact with magnetic field generated by an orbital. Qualitatively, the magnetic field generated by an electron in an orbital is described by

$$\vec{B}_{orb} = -\frac{\vec{v}}{c} \times \vec{E}.$$

And, the electron has a magnetic moment $\mu_e = \dfrac{e}{mc}\vec{S}$, where $\vec{S}$ is a spin operator. Therefore, the Hamiltonian is given by

$$\mathcal{H}_{LS} = -\mu \cdot \vec{B} \cong \vec{\mu} \cdot \left(\frac{\vec{v}}{c} \times \vec{E}\right)$$

$$\Rightarrow \quad \mathcal{H}_{LS} = \frac{1}{2}\frac{e^2}{m^2 c^2 r^3}\vec{L} \cdot \vec{S}$$

where the factor of $\dfrac{1}{2}$ is from the Dirac relativistic theory. Since we can rewrite $\vec{L} \cdot \vec{S}$ as

$$\vec{L} \cdot \vec{S} = \frac{1}{2}\left(J^2 - L^2 - S^2\right),$$

where $\vec{J} = \vec{L} + \vec{S}$, it is more convenient to use a basis formed by $|j, m\rangle$, which are eigenstates of J^2 and J_z. We will denote states of the hydrogen atom using the spectroscopic notation $n^{2s+1}L_j$. There are 6 states with $l = 1$, 4 states of $2^2P_{3/2}$ and 2 states of $2^2P_{1/2}$, and there are 2 states with $l = 1$, $2^2S_{1/2}$.

For example, the first order energy correction for $n = 2$ can be calculated by finding the expectation value of $\vec{L} \cdot \vec{S}$,

$$\langle 2, j, m | \vec{L} \cdot \vec{S} | 2, j, m \rangle = \frac{\hbar^2}{2} \left[j(j+1) - l(l+1) - \frac{3}{4} \right],$$

but $j = l \pm \frac{1}{2}$

$$\Rightarrow \quad \langle 2, j, m | \vec{L} \cdot \vec{S} | 2, j, m \rangle = \frac{\hbar^2}{2} \begin{cases} l & \text{for } j = l + \frac{1}{2} \\ -(l+1) & \text{for } j = l - \frac{1}{2}. \end{cases}$$

This equation is called the Lande's interval rule. The spin-orbit coupling is of the same order as the relativistic effect, which we have considered previous. The last term that we have to consider is called the Darwein term. The Darwin term is due to the jittering motion of the electron over the distance defined by the Compton wavelength $\hbar/m_e c \sim 4 \times 10^{-11}$ cm. The Hamiltonian for the the Darwin is described by

$$\mathcal{H}_{\text{Darwin}} = \frac{\hbar^2}{8 m_e^2 c^2} \nabla^2 V = \frac{\hbar^2}{8 m_e^2 c^2} 4 \pi e^2 \delta(\vec{x}),$$

where V is the Coulomb potential and we note that $\nabla^2 \frac{1}{r} = -4\pi \delta(\vec{x})$. The expectation value of this term is equal to

$$\langle \mathcal{H}_{\text{Darwin}} \rangle = \frac{\hbar^2}{8 m_e^2 c^2} 4 \pi e^2 \frac{1}{4\pi} \frac{4}{n^3} = \frac{1}{2n^3} mc^2 \alpha^4$$

The three results, when conbined, give the following energy correction for the state $|n\rangle$,

$$\boxed{\Delta E_{LS+rel} = -\frac{1}{2} mc^2 \alpha^4 \left[\frac{1}{n^3 \left(j + \frac{1}{2} \right)} - \frac{3}{4n^4} \right].}$$

The splitting of the $n = 2$ energy states due to the fine structure (combined spin-orbit coupling and relativistic correction) is shown in the diagram below
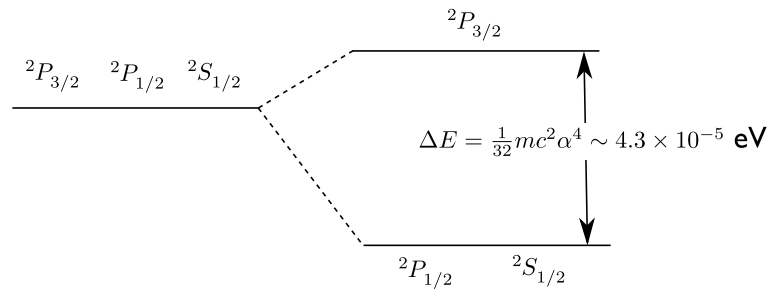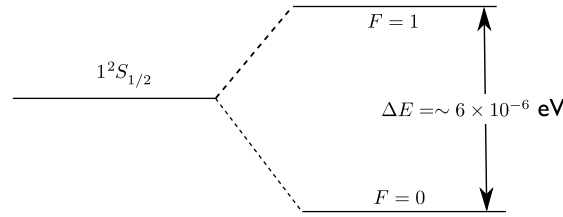

5. **Hyper-fine structure**

The hyper-fine structure is due to the interaction between an electron spin $\vec{S}$ and nuclear spin $\vec{I}$. A total spin is denoted by

$$\vec{F} = \vec{I} + \vec{S}, \quad \frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0.$$

The Hamiltonian is described by

$$H_{HF} \sim \vec{S} \cdot \vec{I} \delta^3(r).$$

The splitting of the ground state $n = 1$ is shown by the diagram below

6. **Zeeman effect** ($\vec{B}-$field)

A magnetic field can interact with both orbital magnetic moment and spin magnetic moment. The former is called the *normal* Zeeman effect and the latter is called the *anomalous* Zeeman effect. The magnetic moment resulting from the orbital angular momentum is described by

$$\mu_{orb} = \frac{IA}{c} = \frac{(ev/2\pi r)\left(\pi r^2\right)}{c} = \frac{e}{2mc}\vec{L}.$$

Therefore, the perturbed potential is given by

$$\mathcal{H}_B = \lambda V = -\frac{e\vec{B}}{2mc}\left(\vec{L} + 2\vec{S}\right) = -\frac{eB}{2mc}\left(L_z + 2S_z\right) = -\frac{eB}{2mc}\left(J_z + S_z\right),$$

where $\vec{B} = B\hat{z}$ and $\vec{J} = \vec{L} + \vec{S}$. We will first use a basis of $|j, m\rangle$. Considering the first-order correction, we need to calculate

$$\langle j, m | J_z + S_z | j, m \rangle = m\hbar + \langle j, m | S_z | j, m \rangle.$$

In order to calculate $\langle S_z \rangle$, we recall the CG coefficients, which we have proven in class

$$\left| j = l \pm \frac{1}{2}, m \right\rangle = \underbrace{\pm\sqrt{\frac{l \pm m + \frac{1}{2}}{2l+1}}}_{C_+}\left| m_l = m - \frac{1}{2}, m_s = \frac{1}{2} \right\rangle + \underbrace{\sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}}}_{C_-}\left| m_l = m + \frac{1}{2}, m_s = -\frac{1}{2} \right\rangle$$

$$\langle S_z \rangle = \frac{\hbar}{2}\left(|C_+|^2 - |C_-|^2\right)$$

$$= \frac{\hbar}{2}\frac{1}{2l+1}\left[\left(l \pm m + \frac{1}{2}\right) - \left(l \mp m + \frac{1}{2}\right)\right] = \pm\frac{m\hbar}{2l+1}$$

$$\Rightarrow \quad \Delta E_B^{(1)} = -\frac{e\hbar B}{2m_e c}m\left(1 \pm \frac{1}{2l+1}\right)$$

This equation is called the Lande's formula for the energy shift due to a magnetic field. However, for a large magnetic field, H_B becomes dominant and $m_l + 2m_s$ becomes a good quantum number. Therefore, the energy shift can be described by

$$\Delta E_B^{(1)} = -\frac{e\hbar B}{2m_e c}\left(m_l + 2m_s\right).$$

The diagram below shows the splitting of eigenenergy for the states $n = 2$ at low field where the spin-orbit coupling $\mathcal{H}_{LS}$ is dominant, and at high field where the Zeeman effect $\mathcal{H}_B$ is dominant.