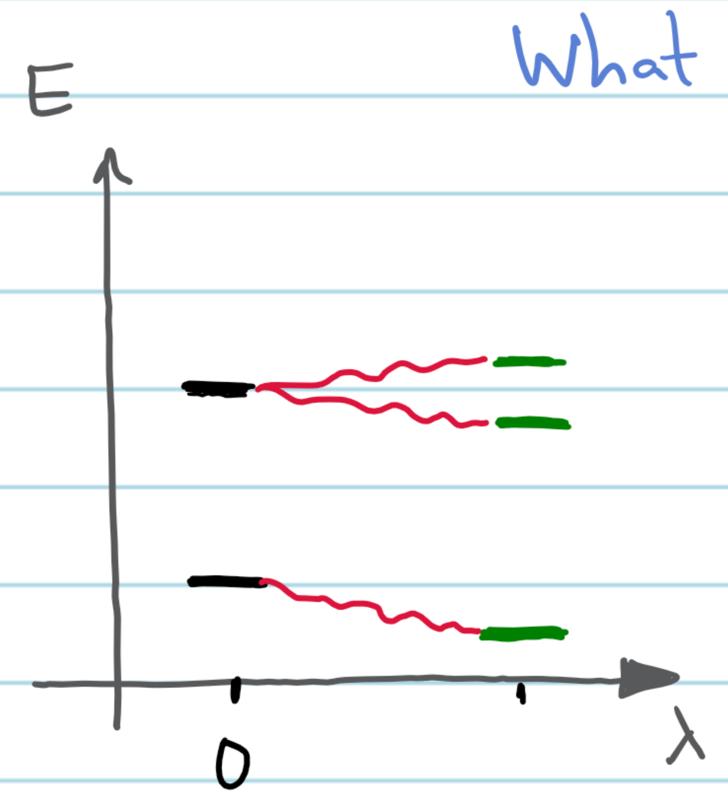
Degenerate Perturbation Theory (DPT)

For the Stark effect, we only considered the ground state $|\phi_{100}\rangle$.

For the excited states $n \geq 2$, the energy is degenerate.

Question: Can we apply NDPT when there's degeneracy?

What are the challenges?



There is an ambiguity when $\lambda \to 0$.

For NDPT: $\lim_{\lambda \to 0} |\phi_n\rangle = |\psi_n^{(0)}\rangle$,

but this is not true if there's degeneracy.

Let's consider the following example:

$$H_0 = E_0 \mathbb{1} \quad , \quad W = E_0 \sigma_x \quad \Rightarrow \quad H = E_0(\mathbb{1} + \lambda \sigma_x)$$

$|\psi_0^{(0)}\rangle = \begin{pmatrix}1\\0\end{pmatrix}$, $|\psi_1^{(0)}\rangle = \begin{pmatrix}0\\1\end{pmatrix}$ but for any $\lambda > 0$: $|\phi_0\rangle = \begin{pmatrix}1\\1\end{pmatrix}/\sqrt{2}$, $|\phi_1\rangle = \begin{pmatrix}1\\-1\end{pmatrix}/\sqrt{2}$.

Also, if we use NDPT, $E_n^{(1)} = 0$ (Verify this!) but if we calculate the $E_n = E_0(1 + (-1)^n \lambda)$ which has a linear term.

The issue has to do with the choice of basis. For $H_0 = E_0 \mathbb{1}$ both $\left\{ \begin{pmatrix}1\\0\end{pmatrix}, \begin{pmatrix}0\\1\end{pmatrix} \right\}$ & $\left\{ \begin{pmatrix}1\\1\end{pmatrix}/\sqrt{2}, \begin{pmatrix}1\\-1\end{pmatrix}/\sqrt{2} \right\}$ form a basis. And this choice would clearly change the result.

Problem Statement

$$H_0 : \begin{bmatrix} E_1^{(0)} & & & & \\ & E_2^{(0)} & & & \\ & & \ddots & & \\ & & & \boxed{E_\ell^{(0)}} & \\ & & & & \ddots \end{bmatrix}$$

$E_\ell \to$ is M times degenerate.

$$\{E_{\ell,1}, E_{\ell,2}, \dots E_{\ell,M}\}$$

$$H = H_0 + \lambda W$$

Also, for simplicity & without lack of generality we move the block of degeneracy to the begining of H_0 & assume that there is only one degenerate eigenenergy.

$$H_0 = \left[\begin{array}{c|c} \boxed{E_1 \mathbb{1}} & 0 \\ \hline 0 & \begin{matrix} E_2 & & \\ & E_3 & \\ & & \ddots \end{matrix} \end{array}\right]$$

Also we refer to the corresponding sub-space as V

$$V = \text{span}\{|\psi_{1,1}^{(0)}\rangle, |\psi_{1,2}^{(0)}\rangle, |\psi_{1,3}^{(0)}\rangle, \dots |\psi_{1,M}^{(0)}\rangle\}.$$

$$E_{1,r}^{(0)} = E_1^{(0)} \quad \forall r$$

Let's consider two situations

1) $W = \Pi_V W \Pi_V + (\mathbb{1} - \Pi_V) W (\mathbb{1} - \Pi_V)$ $\to$ W is block diagonal.

2) (1) is not true. $\to$ W is not block diagonal.

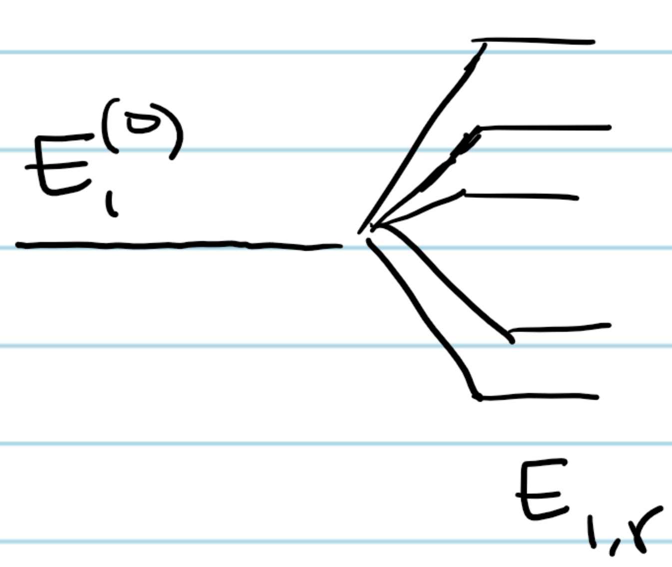
For ① For subspace $\mathcal{V}$: $H_0 = E_1^{(0)} \mathbb{1} \rightarrow W = W_{\mathcal{V}}$

$\rightarrow$ We pick a basis for $\mathcal{V}$ that diagonalizes W

$|\phi_{1,r}\rangle$: $W|\phi_{1,r}\rangle = w_{1,r}|\phi_{1,r}\rangle$

$$\Rightarrow H|\phi_{1,r}\rangle = (H_0 + \lambda W)|\phi_{1,r}\rangle = \underbrace{(E_r^{(0)} + w_{1,r})}_{E_{1,r}}|\phi_{1,r}\rangle$$

The energy is split (if w is not degenerate).



$\rightarrow$ This is not really perturbation.
We solved the problem for $\mathcal{V}$.

For $\bar{\mathcal{V}}$, we use the NDPT.

For (2)

The key is to realize what happens to $\langle \psi_n^{(0)} | \phi_n \rangle$.

Note that $|\psi_{1,r}\rangle$ they all have the same energy.

The first order correction to energy, we get:

$$\rightsquigarrow (H_0 - E_n^{(0)}) |\psi_{n,r}^{(1)}\rangle = (E_{n,r}^{(1)} - W) |\psi_{n,r}^{(0)}\rangle$$

$$\langle \psi_{n,s}^{(0)} | \times \rightsquigarrow \langle \psi_{n,s}^{(0)} | H_0 - E_n^{(0)} | \psi_{n,r}^{(1)} \rangle = \langle \psi_{n,s}^{(0)} | E_{n,r}^{(1)} - W | \psi_{n,r}^{(0)} \rangle$$

$$\Rightarrow \underbrace{(E_n^{(0)} - E_n^{(0)})}_{0} \langle \psi_{n,s}^{(0)} | \psi_{n,r}^{(1)} \rangle = E_{n,r}^{(1)} \delta_{s,r} - \langle \psi_{n,s}^{(0)} | W | \psi_{n,r}^{(0)} \rangle$$

$$\forall r,s \quad \delta_{r,s} E_{n,r}^{(1)} = \langle \psi_{n,s}^{(0)} | W | \psi_{n,r}^{(0)} \rangle \rightarrow W \text{ should be diagonal}$$

in this block. i.e. in V.

$|\psi_{n,r}\rangle$ cannot be arbitrary, it should be such that it makes W diagonal.

$$\Longrightarrow E_{n,r}^{(1)} = \langle \psi_{n,r}^{(0)} | W | \psi_{n,r}^{(0)} \rangle$$

- Degeneracy is lifted by the perturbation if W is not degenerate over V.

  $\rightarrow$ The good basis.

We'll come back to this if W has degeneracy in V.

Diagonalization & finding the basis.

$$\Pi_V W \Pi_V = W_V \xrightarrow{\text{Diagonalize}} U W_V U^\dagger = W_V^D .$$

For the full space, we have

$$\left[\begin{array}{c|c} U & 0 \\ \hline 0 & \mathbb{1} \end{array}\right] \underbrace{W}_{\left[\begin{array}{c|c} W_V & W_{12} \\ \hline W_{21} & W_{\bar V} \end{array}\right]} \left[\begin{array}{c|c} U^\dagger & \\ \hline & \mathbb{1} \end{array}\right] = \left[\begin{array}{c|c} W_V^D & U W_{12} \\ \hline W_{21} U^\dagger & W_{\bar V} \end{array}\right]$$

This means that the unitary $\left[\begin{array}{c|c} U & 0 \\ \hline 0 & \mathbb{1} \end{array}\right]$ gives the right basis for the degenerate subspace, i.e. $\{ |\psi_{1,r}^{(0)}\rangle \mid \langle \psi_{1,r}^{(0)} | W | \psi_{1,s}^{(0)} \rangle \propto \delta_{r,s} \}$.

The State Correction

$$|\psi_{1,r}^{(1)}\rangle = \underbrace{\overbrace{\sum_{s\neq r} \alpha_s |\psi_{1,s}^{(0)}\rangle}^{\text{Within } V}}_{C2} + \underbrace{\overbrace{\sum_{m\neq 1} \beta_m |\psi_m^{(0)}\rangle}^{\text{Outside } V}}_{C1}$$

There are two distinct contributions, one within V and one outside i.e. $\bar V$.

We first find the C1, projection of the correction on $\bar V$

$$\langle \psi_m^{(0)} | \times (P1) \Rightarrow \langle \psi_m^{(0)} | (E_m^{(0)} - E_1^{(0)}) |\psi_{1,r}^{(1)}\rangle = E_n^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_{1,r}^{(0)} \rangle}_{0} - \langle \psi_m^{(0)} | W | \psi_{1,r}^{(0)} \rangle$$

$$\langle \psi_m^{(0)} | \psi_{1,r}^{(1)} \rangle = \frac{\langle \psi_m^{(0)} | W | \psi_{1,r}^{(0)} \rangle}{E_1^{(0)} - E_m^{(0)}}$$

$$|\psi_{1,r}^{(1)}\rangle = \underbrace{\sum_{s\neq r} \alpha_s |\psi_{1,s}^{(0)}\rangle}_{} + \sum_m \frac{\langle \psi_m^{(0)} | W | \psi_{1,r}^{(0)} \rangle}{E_1^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$$

C2 → remains unknown.

The problem: $\langle \psi_m |$ → Gives non-zero contribution on the LHS of the eq., but for $\langle \psi^{(0)}_{1,s} | \psi^{(1)}_{1,r} \rangle$, the eq. P1 is not helpful b/c $\langle \psi_{1,s} | H_0 | \psi_{1,r} \rangle$ is canceled out by $E^{(0)}_1 \langle \psi^{(0)}_{1,s} | \psi^{(1)}_{1,r} \rangle$.

To resolve the issue, we need to go to the next order:

(P2): $$(E^{(0)}_{1,r} - H_0) | \psi^{(2)}_{1,r} \rangle = (E^{(1)}_{1,r} - W) | \psi^{(1)}_{1,r} \rangle + E^{(2)}_{1,r} | \psi^{(0)}_{1,r} \rangle$$

$\langle \psi^{(0)}_{1,s} | \times$, $\boxed{s \neq r}$ → LHS = 0, RHS: $E^{(1)}_{1,r} \langle \psi^{(0)}_{1,s} | \psi^{(1)}_{1,r} \rangle - \underbrace{\langle \psi^{(0)}_{1,s} | W | \psi^{(1)}_{1,r} \rangle} + E^{(2)}_{1,r} \underbrace{\langle \psi^{(0)}_{1,s} | \psi^{(0)}_{1,r} \rangle}_{0}$

We can break this into two parts of $| \psi^{(1)}_{n,r} \rangle$:

$$\langle \psi^{(0)}_{1,s} | W | \psi^{(1)}_{1,r} \rangle = \sum_{q \neq r} \alpha_q \langle \psi^{(0)}_{1,s} | W | \psi^{(0)}_{1,q} \rangle + \sum_m \beta_m \langle \psi^{(0)}_{1,s} | W | \psi^{(0)}_m \rangle$$

We know that $\langle \psi^{(0)}_{1,s} | W | \psi^{(0)}_{1,r} \rangle = \delta_{r,s} E^{(1)}_r$

$$\langle \psi^{(0)}_{1,s} | \psi^{(1)}_{1,r} \rangle E^{(1)}_{1,s} + \sum_m \langle \psi^{(0)}_m | \psi^{(1)}_{1,r} \rangle \langle \psi^{(0)}_{1,s} | W | \psi^{(0)}_m \rangle$$

Putting back into the eq. ⟹

$$(E^{(1)}_{1,r} - E^{(1)}_{1,s}) \langle \psi^{(0)}_{1,s} | \psi^{(1)}_{1,r} \rangle = \sum_{m \neq 1} \langle \psi^{(0)}_m | \psi^{(1)}_{1,r} \rangle \langle \psi^{(0)}_{1,s} | W | \psi^{(0)}_m \rangle$$

$$\langle \psi^{(0)}_{1,s} | \psi^{(1)}_{1,r} \rangle = \sum_{m \neq 1} \frac{\langle \psi^{(0)}_m | W | \psi^{(0)}_{1,r} \rangle}{E^{(0)}_1 - E^{(0)}_m} \frac{\langle \psi^{(0)}_{1,s} | W | \psi^{(0)}_m \rangle}{E^{(1)}_{1,r} - E^{(1)}_{1,s}}$$

This should be non-zero to work. → W should lift the degeneracy.

To recap: $E^{(1)}_{1,r}\langle\psi^{(0)}_{1,s}|\psi^{(1)}_{1,r}\rangle = \langle\psi^{(0)}_{1,s}|W|\psi^{(1)}_{1,r}\rangle$

$$E^{(1)}_{1,r}\langle\psi^{(0)}_{1,s}|\psi^{(1)}_{1,r}\rangle = \langle\psi^{(0)}_{1,s}|W\overbrace{(\Pi_{V}+\Pi_{\bar{V}})}^{\mathbb{1}}|\psi^{(1)}_{1,r}\rangle$$

$$E^{(1)}_{1,r}\langle\psi^{(0)}_{1,s}|\psi^{(1)}_{1,r}\rangle = \underbrace{\langle\psi^{(0)}_{1,s}|W\left(\Pi_{V}|\psi^{(1)}_{1,r}\rangle\right)}_{E^{(1)}_{1,s}\langle\psi^{(0)}_{1,s}|\psi^{(1)}_{1,r}\rangle} + \langle\psi^{(0)}_{1,s}|W\left(\Pi_{\bar{V}}|\psi^{(1)}_{1,r}\rangle\right)$$

$r\neq s$

$$\Rightarrow \langle\psi^{(0)}_{1,s}|\psi^{(1)}_{1,r}\rangle = \frac{\langle\psi^{(0)}_{1,s}|W\,\Pi_{\bar{V}}|\psi^{(1)}_{1,r}\rangle}{E^{(1)}_{1,r} - E^{(1)}_{1,s}}$$

Note that everything on the RHS is known, either from λ^1 or from λ^0 equations (i.e. the zeroth & first order terms).

* Question: What happens if W has degeneracy in V and does not lift the degeneracy of state (at least not completely)?

Second order

$$(E_1^{(0)} - H_0)|\psi_{1,r}^{(2)}\rangle = (E_{1,r}^{(1)} - W)|\psi_{1,r}^{(1)}\rangle + E_{1,r}^{(2)}|\psi_{1,r}^{(0)}\rangle$$

$$\langle\psi_{1,r}^{(0)}| \times \to \quad 0 = E_{1,r}^{(1)} \underbrace{\langle\psi_{1,r}^{(0)}|\psi_{1,r}^{(1)}\rangle}_{0} - \langle\psi_{1,r}^{(0)}|W|\psi_{1,r}^{(1)}\rangle + E_{1,r}^{(2)} \underbrace{\langle\psi_{1,r}^{(0)}|\psi_{1,r}^{(0)}\rangle}_{1}$$

$$\Rightarrow E_{1,r}^{(2)} = \langle\psi_{1,r}^{(0)}|W|\psi_{1,r}^{(1)}\rangle =$$

$$\underbrace{\langle\psi_{1,r}^{(0)}|W(\Pi_V|\psi_{1,r}^{(1)}\rangle)}_{E_{1,r}^{(1)}\underbrace{\langle\psi_{1,r}^{(0)}|\psi_{1,r}^{(1)}\rangle}_{0}} + \langle\psi_{1,r}^{(0)}|W(\underbrace{\Pi_{\bar{V}}|\psi_{1,r}^{(1)}\rangle}_{\sum_{m\neq 1}\frac{\langle\psi_m^{(0)}|W|\psi_{1,r}^{(0)}\rangle}{E_1^{(0)}-E_m^{(0)}}|\psi_m^{(0)}\rangle})$$

$$E_{1,r}^{(2)} = \sum_{m\neq 1} \frac{|\langle\psi_{1,r}^{(0)}|W|\psi_m^{(0)}\rangle|^2}{E_1^{(0)} - E_m^{(0)}}$$

Degenerate W_V :

That is $\langle \psi^{(0)}_{1,s} | W | \psi^{(0)}_{1,r} \rangle = \boxed{E^{(0)}_1} \delta_{r,s}$

The same for all r values.

The eq. above gives the first order correction to E_1 which is the same for all r.

Let's assume that the vectors are $|\psi^{(0)}_{1,r}\rangle$.

What are these?

To the first order:

(*) $$\langle \psi^{(0)}_m | \psi^{(1)}_{1,r} \rangle = \frac{W_{m,(1r)}}{E^{(0)}_1 - E^{(0)}_m}$$ → This still doesn't say much.

2nd order

$$\langle \psi^{(0)}_{1,s} | \times \to 0 = \langle \psi^{(0)}_{1,s} | (E^{(1)}_n - W) | \psi^{(1)}_{1,r} \rangle + E^{(2)}_{1,r} \langle \psi^{(0)}_{1,s} | \psi^{(0)}_{1,r} \rangle$$

This can be simplified to

(**) $$\langle \psi^{(0)}_{1,s} | W \Pi_V | \psi^{(1)}_{1,r} \rangle = E^{(2)}_{1,r} \langle \psi^{(0)}_{1,s} | \psi^{(0)}_{1,r} \rangle$$

The two equations (*) & (**) would give the $|\psi^{(0)}_{1,r}\rangle$. This means that we need to go to second order to find the right basis.