Approximation Methods in QM

In most state-of-the-art research problems, it is almost impossible to solve the Schrödinger equation exactly. To move forward, we need to use approximation methods. Generally, we can divide them into two classes:

<table>
<thead>
<tr>
<th>Perturbative</th>
<th>Non-perturbative</th>
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<tbody>
<tr>
<td>$\hat{A} = \hat{A}_0 + \alpha \hat{A}_1$</td>
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<tr>
<td>with $\alpha \hat{A}_1 \Rightarrow \text{``small''}$</td>
<td>- variational</td>
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<td>and $\hat{A}_0 \Rightarrow \text{``solvable''}$</td>
<td>- Semiclassical/MBMB</td>
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<td>Time-independent</td>
<td>Adiabatic methods and Landau-Zener theory</td>
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<td>$\Rightarrow$ Non-degenerate</td>
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<td>$\Rightarrow$ Degenerate</td>
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<td>Time-dependent</td>
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<td>$\Rightarrow$ general theory</td>
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<td>$\Rightarrow$ Periodic time-dependence:</td>
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<td>* Fermi-Golden rule</td>
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<td>* Floquet</td>
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<td>* Rotating wave</td>
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Time-independent perturbation theory:

Let $\hat{A} = \hat{A}_0 + \hat{A}_1$ where $\hat{A}_1 = \text{``small''}$

Assume $\hat{A}_0$ has a complete, orthonormal set of eigenvalues $E^n$ and eigenstates $|\psi^n\rangle$.

* Case I: Spectrum of $\hat{A}_0$ is discrete, non-degenerate.

$\Rightarrow$ This treatment is called Rayleigh-Schrödinger perturbation theory.
\( \mathcal{E} \) is assumed to be real, "small number".

We also assume we \( \hat{H}_0 \) is exactly solvable:

\[ \hat{H}_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \]

\( \Rightarrow \) We want to find \( |\psi_n\rangle \) and \( E_n \), such that

\[ \hat{A} |\psi_n\rangle = E_n |\psi_n\rangle \quad (1) \]

Since \( \mathcal{E} \) is a small parameter we can expand \( |\psi_n\rangle \) in powers of \( \mathcal{E} \)

\( \Rightarrow \) We make an ansatz of the form:

\[ |\psi_n\rangle = |\psi_n^{(w)}\rangle + \mathcal{E} |\psi_n^{(1)}\rangle + \mathcal{E}^2 |\psi_n^{(2)}\rangle + \cdots \quad (2) \]

and

\[ E_n = E_n^{(w)} + \mathcal{E} E_n^{(1)} + \mathcal{E}^2 E_n^{(2)} + \cdots \quad (3) \]

In words: \( |\psi_n^{(w)}\rangle \) is the part of \( |\psi_n\rangle \) that is \( \mathcal{E} \)-th order in the perturbation \( \mathcal{E} \).

Here we are using \( \mathcal{E} \) as a "book-keeping" tool for our derivation and we will eventually set \( \mathcal{E} \to 1 \)

\( \Rightarrow \) To solve for \( |\psi_n^{(w)}\rangle \) we have to plug (2) and (3) into (1) and equate equal powers of \( \mathcal{E} \).

\[ (\hat{H}_0 + \mathcal{E}\hat{A})\left( |\psi_n^{(w)}\rangle + \mathcal{E} |\psi_n^{(1)}\rangle + \mathcal{E}^2 |\psi_n^{(2)}\rangle + \cdots \right) = (E_n^{(w)} + \mathcal{E} E_n^{(1)} + \mathcal{E}^2 E_n^{(2)} + \cdots) \]

Now let's try to collect terms of equal order in \( \mathcal{E} \)

<table>
<thead>
<tr>
<th>Order in ( \mathcal{E} )</th>
<th>Equality from Eq. (4)</th>
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<tbody>
<tr>
<td>0</td>
<td>( \hat{H}_0</td>
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</table>
1. $\hat{H}_0 \psi_n^{(n)} + V \psi_n^{(n)} = E_n^{(n)} \psi_n^{(n)} + \epsilon_n^{(n)} \psi_n^{(n)} \quad (5)$

2. $\hat{H}_0 \psi_n^{(n)} + V \psi_n^{(n)} = E_n^{(n)} \psi_n^{(n)} + \epsilon_n^{(n)} \psi_n^{(n)} + E_n^{(n)} \psi_n^{(n)} \quad (7)$

\[ \vdots \]

`etc`

**First-Order Treatment:**

Since $\{\psi_n^{(n)}\}$ are a complete set, we can expand $\psi_n^{(n)}$ in terms of them:

\[ \psi_n^{(n)} = \sum_i \psi_i^{(n)} c_n^{(i)} \quad (7) \]

Plugging (7) into (5) gives:

\[ \hat{H}_0 \left( \sum_i \psi_i^{(n)} c_n^{(i)} \right) + V \psi_n^{(n)} = E_n^{(n)} \sum_i \psi_i^{(n)} c_n^{(i)} + \epsilon_n^{(n)} \psi_n^{(n)} \]

Now let's apply $\langle \psi_j^{(n)} \rangle$ from the left and use the orthonormality of the eigenstates:

\[ \sum_i \langle \psi_j^{(n)} | \psi_i^{(n)} \rangle c_n^{(i)} + \langle \psi_j^{(n)} | V \psi_n^{(n)} \rangle = E_n^{(n)} \sum_i \delta_{ji} c_n^{(i)} + E_n^{(n)} \delta_{jn} \]

$v_{jn}$: abbreviation

Let's consider two cases:

\[ j=n \text{ case } \Rightarrow E_n^{(n)} c_n^{(n)} + V_{nn} = E_n^{(n)} c_n^{(n)} + \epsilon_n^{(n)} \]

So

\[ E_n^{(n)} = V_{nn} \quad \text{Note: no info about} \quad c_n^{(n)} \]

\[ j \neq n \text{ case } \Rightarrow E_j^{(n)} c_n^{(i)} + V_{jn} = E_n^{(n)} c_n^{(i)} \]
\[ j \pm n \text{ case } \Rightarrow E_i C_{n^j} + V_{jn} = E_{n^j} C_{n^j} \]

\[ C_{n^j} = \frac{V_{jn}}{E_{n^j} - E_{i^j}} \]

So to first order in \( x \), we obtain:

\[ E_n = E_n^{(0)} + \gamma \left\langle \psi_n^{(0)} \vert V \vert \psi_n^{(0)} \right\rangle \quad \text{and} \]

\[ \vert \psi_n \rangle = \vert \psi_n^{(0)} \rangle + \gamma \sum_{i \neq n} \frac{1}{E_{n}^{(0)} - E_{i}^{(0)}} \left( \left\langle \psi_i^{(0)} \vert V \vert \psi_n^{(0)} \right\rangle + 2 C_{n^i} \vert \psi_n^{(0)} \rangle \right) \]

Normalization conditions impose:

\[ \left\langle \psi_n \vert \psi_n \right\rangle = 1 = \left| 1 + \gamma \sum_{i \neq n} C_{n^i} \right|^2 + \gamma^2 \sum_{i \neq n} \frac{|V_{ni}|^2}{(E_{n}^{(0)} - E_{i}^{(0)})^2} \]

From the above equation it is clear that \( C_{n^i} \) is set to fix the normalization condition and to \( 1^{\text{st}}\)-order in \( \gamma \), it can be choose to be \( C_{n^i} = 0 \), and thus

\[ \vert \psi_n \rangle = \vert \psi_n^{(0)} \rangle + \gamma \sum_{i \neq n} \frac{V_{ni}}{E_{n}^{(0)} - E_{i}^{(0)}} \left\langle \psi_i \vert \psi_n \right\rangle \]

\textbf{Comments}

(i) The \( 1^{\text{st}}\)-order correction of \( E_n^{(0)} \) is simply the expectation value of \( V \) in the state \( \vert \psi_n^{(0)} \rangle \)

(ii) The corrected wave function \( \vert \psi_n \rangle \) is found by adding to \( \vert \psi_n^{(0)} \rangle \) all the \( \vert \psi_i^{(0)} \rangle \), i.e. each weighted by \( \frac{V_{ni}}{(E_{n}^{(0)} - E_{i}^{(0)})} \).

Because of the denominator, close-energy states tend to have a greater effect.
Second-order treatment

Similarly we can expand $|\psi_{(2)}\rangle = \sum_i |\psi_i^{(1)}\rangle |C_n\rangle$.

Then

$\sum_i \int_0^1 |\psi_i^{(1)}\rangle \langle C_n| V_0 |\psi_i^{(0)}\rangle |C_n\rangle =

\sum_i |\psi_i^{(0)}\rangle \langle C_n| V_0 |\psi_i^{(0)}\rangle |C_n\rangle + \sum_i |\psi_i^{(0)}\rangle \langle C_n| E_n^{(2)} |\psi_i^{(0)}\rangle |C_n\rangle$

Again apply $|\psi_j^{(0)}\rangle$ then

$E_j^{(0)} |C_n\rangle + \sum_i V_{ji} |C_n\rangle = E_n^{(1)} |C_n\rangle + E_n^{(2)} |C_n\rangle + E_j^{(0)} |\psi_j^{(0)}\rangle$

Two cases this time too:

1. $n = j$

$E_n^{(2)} |C_n\rangle + \sum_i V_{ni} |C_n\rangle = E_n^{(2)} |C_n\rangle + E_n^{(2)} |C_n\rangle + E_n^{(2)}$

$= E_n^{(0)} - \sum_i V_{ni} |C_n\rangle$

So the 2nd-order perturbation correction is

$E_n^{(2)} = \sum_{i \neq n} \frac{|V_{ni}|^2}{E_n^{(0)} - E_i^{(0)}}$

So the full energy expression to 2nd order in $V$ is (setting $a$ to $2$)

$E_n = E_n^{(0)} + V_{nn} + \sum_{i \neq n} \frac{|V_{ni}|^2}{E_n^{(0)} - E_i^{(0)}}$

You can solve the $j \neq n$ case on your own if you need to go second order in eigenstates too.

Remarks:
1. If \( E_n^{(0)} \) is the ground state energy, then the 2nd-order correction wants to lower the energy: \( E_n^{(2)} < 0 \).

2. Usually the most important terms in the sum for \( E_n^{(2)} \) (and for \( H_n^{(3)} \)) are the ones close in energy.

3. The sums over \( i \) in \( E_n^{(2)} \) and \( H_n^{(3)} \) must be understood to include an integral over the energy continuum in addition to a discrete sum over bound states.

4. If two levels \( n, n' \) are close in energy and \( V_{nn'} \neq 0 \), then the lower level will be pushed down by the 2nd-order \( V \), whereas the upper level is pushed up.

\[
\begin{align*}
E_n^{(0)} + V_{nn'} & \rightarrow E_n' \\
E_n^{(0)} + V_{nn} & \rightarrow E_n
\end{align*}
\]

This effect is called "Level Repulsion."

Visualization of perturbation theory

The matrix of \( \hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{W}} \) in a basis where \( \hat{\mathcal{H}}_0 \) is diagonal looks like:

\[
\hat{\mathcal{H}} = \begin{bmatrix}
E_1^{(0)} & 0 \\
0 & E_2^{(0)} \\
0 & \ddots & \ddots
\end{bmatrix} + \begin{bmatrix}
V_{11} & V_{12} & \cdots \\
V_{21} & V_{22} & \cdots \\
\vdots & \vdots & \ddots
\end{bmatrix}
\]

i.e \( H_{ij} = E_i^{(0)} \delta_{ij} + V_{ij} \)
Note that the diagonal elements in $\hat{A}$ give the energies in 1st-order and in 2nd order perturbation theory. The effects of the off-diagonal terms are accounted for.

The criterion for validity of perturbation theory for state $n$ is

$$\left| \frac{V_{cn}}{E^{(0)}_n - E^{(0)}_c} \right| \ll 1 \quad \text{for all states } c$$

A key point: The above perturbation fails if

$$E^{(0)}_n = E^{(0)}_c \quad \text{for some } c, \text{ unless } V_{cn} = 0$$

This issue leads naturally to a way to formulate DEGENERATE PERTURBATION THEORY

Suppose there are $N$ degenerate states (zero order) $|\psi_i\rangle, \ i = 1, \ldots, N$

which are coupled by the perturbation $\hat{V}$ that is non-zero in this subspace

Since the method of non-degenerate perturbation theory fails, we need a different approach

First note that: Since the $|\psi_i\rangle$ are degenerate and obey

$$\hat{A}_0 |\psi_i\rangle = E^{(0)}_i |\psi_i\rangle \quad (\ast)$$

This means that any linear combination of the $|\psi_i\rangle$ will still satisfy Eq (\ast)
Solution: We just need to find those linear combinations of \( |\psi_i\rangle \) such that the off-diagonal elements of \( \hat{V} \) vanish in the new representation.

In other words we want to find a unitary transformation to a set of new states \( |\psi_i\rangle \equiv |\varphi_i\rangle |\psi_i\rangle \) (i.e. \( C_{mi} = \langle \varphi_i | \psi_m \rangle \)) and demand that \( \langle \psi_m | \hat{V} | \psi_n \rangle = 0 \) for \( m \neq n \).

This is accomplished if we simply diagonalize the matrix \( \langle \varphi_i | \hat{V} | \varphi_j \rangle \equiv V_{ij} \).

Explicitly we need to solve

\[
\sum_j V_{ij} C_{mj} = C_{mi} \omega_m
\]

or

\[
\hat{V} \overline{C}_m = \omega_m \overline{C}_m
\]

where \( \omega_m = \mu^{\text{-th}} \) eigenvalue

\( \overline{C}_m = \mu^{\text{-th}} \) eigenstate

And then the first order perturbed eigenvalues are

\[
E_m = E_0 + \omega_m \quad m = 1, \ldots, N
\]

Possible simplification: Sometimes \( H \) is block-diagonal in some quantum numbers and the calculations simplify enormously using this fact. Let's work some examples.