CHM 502 - Module 5 - Time-Independent Perturbation Theory

Prof. Marissa Weichman

Many important problems in quantum mechanics cannot be solved exactly. In these cases, perturbation theory (PT) is an important tool. To capture light-matter interactions and spectroscopy, we will ultimately use time-dependent perturbation theory, but we will first build up our mathematical formalism using time-independent perturbation theory. Time-independent perturbation theory comes in two flavors: non-degenerate (when all the eigenvalues are distinct) and degenerate (when some eigenvalues may be identical).

1 Non-degenerate perturbation theory

1.1 Laying out the problem

Imagine that we have a reference Hamiltonian $\hat{H}^{(0)}$, where we have already solved the time-independent Schrödinger equation to find its energy eigenvectors $\{|\psi_j^{(0)}\rangle\}$ and eigenvalues $\{E_j^{(0)}\}$. We will call these the "zeroth-order" solutions.

We then consider slightly perturbing our Hamiltonian:

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)} \tag{1}$$

where $\hat{H}^{(1)}$ is a "small" perturbation. The λ coefficient is just there for bookkeeping purposes, as we will see shortly. The idea here is that the solutions to $\hat{H}$, which we will call $\{|\psi_j\rangle\}$ and $\{E_j\}$ will not be too different from the solutions to our known reference system.

The scale for what is considered small is typically the energy level separations of $\hat{H}^{(0)}$. Some examples of problems that can be treated within a small perturbation picture include $L \cdot S$ coupling in light atoms, anharmonic oscillators, and the static Stark and Zeeman effects.
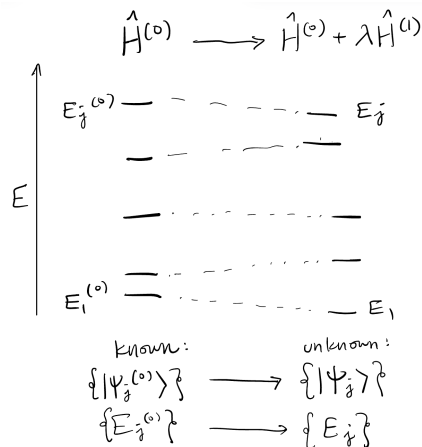
Our goal here is to understand how this new perturbed system behaves by finding the unknown $\{|\psi_j\rangle\}$ and $\{E_j\}$ solutions in terms of known quantities, including our $\{|\psi_j^{(0)}\rangle\}$ and $\{E_j^{(0)}\}$ solutions.

We will do this by first defining power series expansions for the solutions to $\hat{H}$ in powers of λ:

$$\hat{H}|\psi_j(\lambda)\rangle = E_j(\lambda)|\psi_j(\lambda)\rangle \tag{2}$$

$$E_j(\lambda) = E_j^{(0)} + \lambda E_j^{(1)} + \frac{1}{2}\lambda^2 E_j^{(2)} + \cdots \tag{3}$$

$$|\psi_j(\lambda)\rangle = |\psi_j^{(0)}\rangle + \lambda|\psi_j^{(1)}\rangle + \frac{1}{2}\lambda^2|\psi_j^{(2)}\rangle + \cdots \tag{4}$$

where $E_j^{(1)}, E_j^{(2)}, \ldots$ and $|\psi_j^{(1)}\rangle, |\psi_j^{(2)}\rangle, \ldots$ are expansion coefficients to be determined in terms of known quantities: our reference Hamiltonian $\hat{H}^{(0)}$, the perturbation $\hat{H}^{(1)}$, and our reference eigenvectors and eigenvalues $E_j^{(0)}$ and $|\psi_j^{(0)}\rangle$.

For first-order PT, we can truncate these series at the first power of λ, for second-order PT, we keep terms up to λ^2, etc.

Here is a roadmap (and cheat sheet!) for how we will find the expansion coefficients:

1. Plug in our expansions for $|\psi_j(\lambda)\rangle$ and $E_j(\lambda)$ into the time-independent Schrödinger equation:

$$\hat{H}(\lambda)|\psi_j(\lambda)\rangle = E_j(\lambda)|\psi_j(\lambda)\rangle \tag{5}$$

2. Group terms of Eqn. 5 by powers of λ.

3. Left-project our first-order expression from the previous step with a reference bra $\langle\psi_j^{(0)}|$ and simplify.

4. Rearrange to find

$$\boxed{E_j^{(1)} = \langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(0)}\rangle} \tag{6}$$

5. Plug expression for $E_j^{(1)}$ from previous step into first-order expression and solve for $|\psi_j^{(1)}\rangle = \sum_k c_{kj}^{(1)}|\psi_k^{(0)}\rangle$, while ensuring that the wavefunctions are normalized. It will turn out that

$$\boxed{c_{kj}^{(1)} = \frac{\hat{H}_{kj}^{(1)}}{E_j^{(0)} - E_k^{(0)}}} \tag{7}$$

6. Then turn to the second-order expression from Eqn. 5 and recursively find the second-order expansion coefficients in terms of the zeroth-order and first-order solutions. For instance, you will find

$$\boxed{E_j^{(2)} = \sum_{k \neq j} \frac{\hat{H}_{jk}^{(1)} \cdot \hat{H}_{kj}^{(1)}}{E_j^{(0)} - E_k^{(0)}}} \tag{8}$$

1.2 Grouping terms in the Schrödinger equation by λ

We begin by substituting Eqns. 3 and 4 above into the time-independent Schrödinger equation:

$$\hat{H}|\psi_j(\lambda)\rangle = E_j(\lambda)|\psi_j(\lambda)\rangle \tag{9}$$

$$\text{RHS:} \quad \left(\hat{H}^{(0)} + \lambda\hat{H}^{(1)}\right)\left(|\psi_j^{(0)}\rangle + \lambda|\psi_j^{(1)}\rangle + \frac{1}{2}\lambda^2|\psi_j^{(2)}\rangle + \cdots\right) \tag{10}$$

$$\text{LHS:} \quad \left(E_j^{(0)} + \lambda E_j^{(1)} + \frac{1}{2}\lambda^2 E_j^{(2)} + \cdots\right)\left(|\psi_j^{(0)}\rangle + \lambda|\psi_j^{(1)}\rangle + \frac{1}{2}\lambda^2|\psi_j^{(2)}\rangle + \cdots\right) \tag{11}$$

The above expression can only hold true for arbitrary values of λ if the coefficients of each power of λ are equivalent on both right and left hand sides. So, grouping in powers of λ:

$$\underline{\underline{\lambda^0}}: \quad \hat{H}^{(0)}|\psi_j^{(0)}\rangle = E_j^{(0)}|\psi_j^{(0)}\rangle \quad \checkmark \quad \text{our solved reference problem} \tag{12}$$

$$\underline{\underline{\lambda^1}}: \quad \hat{H}^{(0)}|\psi_j^{(1)}\rangle + \hat{H}^{(1)}|\psi_j^{(0)}\rangle = E_j^{(0)}|\psi_j^{(1)}\rangle + E_j^{(1)}|\psi_j^{(0)}\rangle \tag{13}$$

$$\underline{\underline{\lambda^2}}: \quad \hat{H}^{(1)}|\psi_j^{(1)}\rangle + \frac{1}{2}\hat{H}^{(0)}|\psi_j^{(2)}\rangle = \frac{1}{2}E_j^{(2)}|\psi_j^{(0)}\rangle + E_j^{(1)}|\psi_j^{(1)}\rangle + \frac{1}{2}E_j^{(0)}|\psi_j^{(2)}\rangle \tag{14}$$

$$\cdots$$

It's clear that this is a recursive problem. We can find the first-order quantities $E_j^{(1)}$ and $|\psi_j^{(1)}\rangle$ in terms of the known zeroth-order eigenvalues and eigenfunctions. The second-order quantities can be expressed in terms of known zeroth- and first-order quantities, etc.

1.3 First-order corrections to the energy eigenvalues

We can consider just the first-order quantities by projecting our first-order expression in Eqn. 13 with $\langle\psi_j^{(0)}|$ from the left:

$$\langle\psi_j^{(0)}|\hat{H}^{(0)}|\psi_j^{(1)}\rangle + \langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(0)}\rangle = \langle\psi_j^{(0)}|E_j^{(0)}|\psi_j^{(1)}\rangle + \langle\psi_j^{(0)}|E_j^{(1)}|\psi_j^{(0)}\rangle \tag{15}$$

$$= E_j^{(0)}\cancel{\langle\psi_j^{(0)}|\psi_j^{(1)}\rangle} + \langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(0)}\rangle = E_j^{(0)}\cancel{\langle\psi_j^{(0)}|\psi_j^{(1)}\rangle} + E_j^{(1)}\langle\psi_j^{(0)}|\psi_j^{(0)}\rangle \tag{16}$$

$$\rightarrow \quad \boxed{E_j^{(1)} = \langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(0)}\rangle} \tag{17}$$

Note the identical terms which we cancel on the left and right-hand sides.

The diagonal elements of $\hat{H}^{(1)}$ therefore give us the first-order corrections to the energy $E_j^{(1)}$. To solve this problem to first order, there is no need to diagonalize $\hat{H}^{(1)}$!

Aside: To give a concrete example, say we have a 1D harmonic oscillator (HO) with $\hat{H}^{(0)} = \hat{KE} + \frac{1}{2}kx^2$. We might consider the quartic oscillator as a perturbation, with $\hat{H}^{(1)} = \lambda cx^4$. Provided λ is small, we expect that the jth new energy level will diverge from the original j^{th} HO energy level by $\sim E_j^{(1)} = \lambda c\langle\psi_j^{(0)}|x^4|\psi_j^{(0)}\rangle$.

1.4   First-order corrections to the energy eigenfunctions

We now consider $|\psi_j^{(1)}\rangle$, the first-order corrections to our eigenfunctions. Let's return to our λ^1 expression in Eqn. 13. Since we have now found $E_j^{(1)}$, we only have one remaining unknown:

$$\hat{H}^{(0)}|\psi_j^{(1)}\rangle + \hat{H}^{(1)}|\psi_j^{(0)}\rangle = E_j^{(0)}|\psi_j^{(1)}\rangle + E_j^{(1)}|\psi_j^{(0)}\rangle \tag{18}$$

$|\psi_j^{(1)}\rangle$ can be expressed as an expansion of our zeroth-order wavefunctions (which form a complete, orthonormal basis set):

$$|\psi_j^{(1)}\rangle = \sum_k c_{kj}^{(1)}|\psi_k^{(0)}\rangle \tag{19}$$

Aside: Before we go further, it's useful to require that our wavefunction remain normalized:

$$\langle\psi_j(\lambda)|\psi_j(\lambda)\rangle = 1 \tag{20}$$

$$\text{where } |\psi_j(\lambda)\rangle = |\psi_j^{(0)}\rangle + \lambda|\psi_j^{(1)}\rangle + \frac{1}{2}\lambda^2|\psi_j^{(2)}\rangle + \cdots \tag{21}$$

This implies

$$\left[\langle\psi_j^{(0)}| + \lambda\langle\psi_j^{(1)}| + \frac{1}{2}\lambda^2\langle\psi_j^{(2)}| + \cdots\right]\left[|\psi_j^{(0)}\rangle + \lambda|\psi_j^{(1)}\rangle + \frac{1}{2}\lambda^2|\psi_j^{(2)}\rangle + \cdots\right] = 1 \tag{22}$$

Let's use our trusty trick of grouping by powers of λ. We know that all coefficients multiplying factors of λ must go to zero if we want Eqn. 22 to evaluate to 1 for arbitrary λ:

$$\underline{\underline{\lambda^0}}: \quad \langle\psi_j^{(0)}|\psi_j^{(0)}\rangle = 1 \tag{23}$$

$$\underline{\underline{\lambda^1}}: \quad \langle\psi_j^{(0)}|\psi_j^{(1)}\rangle + \langle\psi_j^{(1)}|\psi_j^{(0)}\rangle = 0 \tag{24}$$

$$\underline{\underline{\lambda^2}}: \quad \frac{1}{2}\langle\psi_j^{(0)}|\psi_j^{(2)}\rangle + \frac{1}{2}\langle\psi_j^{(2)}|\psi_j^{(0)}\rangle + \langle\psi_j^{(1)}|\psi_0^{(1)}\rangle = 0 \tag{25}$$

Note that in the λ^1 expression, if the $\langle\psi_0^{(0)}|\psi_0^{(1)}\rangle$ product is real, $|\psi_0^{(0)}\rangle$ and $|\psi_0^{(1)}\rangle$ must be orthogonal. Without loss of generality, we can choose $\langle\psi_0^{(0)}|\psi_0^{(1)}\rangle$ to be real, and therefore take $c_{kk}^{(1)} = 0$. In other words, $|\psi_j^{(1)}\rangle$ has no contribution from the zeroth-order eigenfunction with the same index j:

$$|\psi_j^{(1)}\rangle = \sum_{k \neq j} c_{kj}^{(1)}|\psi_k^{(0)}\rangle \tag{26}$$

Making this choice ensures our wavefunction is normalized, at least to first order.

The other $c_{kj}^{(1)}$ coefficients can be found by projecting Eqn. 18 with $\langle\psi_k^{(0)}|$:

$$\langle\psi_k^{(0)}|\,\hat{H}^{(0)}\,|\psi_j^{(1)}\rangle + \langle\psi_k^{(0)}|\,\hat{H}^{(1)}\,|\psi_j^{(0)}\rangle = \langle\psi_k^{(0)}|\,E_j^{(0)}|\,|\psi_j^{(1)}\rangle + \langle\psi_k^{(0)}|\,E_j^{(1)}\,|\psi_j^{(0)}\rangle \tag{27}$$

$$\langle\psi_k^{(0)}|\,\hat{H}^{(0)}\sum_{m\neq j} c_{mj}^{(1)}\,|\psi_m^{(0)}\rangle + \langle\psi_k^{(0)}|\hat{H}^{(1)}|\psi_j^{(0)}\rangle = \langle\psi_k^{(0)}|\,E_j^{(0)}|\sum_{m\neq j} c_{mj}^{(1)}\,|\psi_m^{(0)}\rangle + \langle\psi_k^{(0)}|E_j^{(1)}|\psi_j^{(0)}\rangle \tag{28}$$

$$= \sum_{m\neq j} c_{mj}^{(1)}\overbrace{\langle\psi_k^{(0)}|\hat{H}^{(0)}|\psi_m^{(0)}\rangle}^{\delta_{km}E_k^{(0)}} + \hat{H}_{kj}^{(1)} = E_j^{(0)}\sum_{m\neq j} c_{mj}^{(1)}\overbrace{\langle\psi_k^{(0)}|\psi_m^{(0)}\rangle}^{\delta_{km}} + E_j^{(1)}\overbrace{\langle\psi_k^{(0)}|\psi_j^{(0)}\rangle}^{0} \tag{29}$$

$$= c_{kj}^{(1)}E_k^{(0)} + \hat{H}_{kj}^{(1)} = E_j^{(0)}c_{kj}^{(1)} \tag{30}$$

$$\rightarrow \boxed{c_{kj}^{(1)} = \frac{\hat{H}_{kj}^{(1)}}{E_j^{(0)} - E_k^{(0)}}} \tag{31}$$

And thus we have found the kth expansion coefficient of $|\psi_j^{(1)}\rangle = \sum_k c_{kj}^{(1)}\,|\psi_k^{(0)}\rangle$.

1.5   Second-order quantities

It's not much more work to find the second-order correction to the energy eigenvalues, $E_j^{(2)}$. This time we will take our λ^2 expression in Eqn. 14 and project with $\langle\psi_j^{(0)}|$:

$$\langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(1)}\rangle + \frac{1}{2}\langle\psi_j^{(0)}|\hat{H}^{(0)}|\psi_j^{(2)}\rangle = \frac{E_j^{(2)}}{2}\langle\psi_j^{(0)}|\psi_j^{(0)}\rangle + E_j^{(1)}\overbrace{\langle\psi_j^{(0)}|\psi_j^{(1)}\rangle}^{0} + \frac{E_j^{(0)}}{2}\langle\psi_j^{(0)}|\psi_j^{(2)}\rangle \tag{32}$$

$$= \langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(1)}\rangle + \frac{E_j^{(0)}}{2}\cancel{\langle\psi_j^{(0)}|\psi_j^{(2)}\rangle} = \frac{E_j^{(2)}}{2} + \frac{E_j^{(0)}}{2}\cancel{\langle\psi_j^{(0)}|\psi_j^{(2)}\rangle} \tag{33}$$

$$\rightarrow \boxed{E_j^{(2)} = \langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(1)}\rangle} \tag{34}$$

Since the second-order correction to the energy involves the first-order correction to the ground state wavefunction, our solution will depend on *all* zeroth-order energies:

$$\frac{1}{2}\lambda^2 E_j^{(2)} = \lambda^2\langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(1)}\rangle \tag{35}$$

$$= \lambda^2\sum_{k\neq j} c_{kj}^{(1)}\langle\psi_j^{(0)}|\hat{H}^{(1)}|\psi_j^{(0)}\rangle \tag{36}$$

$$= \lambda^2\sum_{k\neq j} c_{kj}^{(1)}\hat{H}_{jk}^{(1)} \tag{37}$$

$$= \boxed{\lambda^2\sum_{k\neq j}\frac{\hat{H}_{jk}^{(1)}\cdot\hat{H}_{kj}^{(1)}}{E_j^{(0)} - E_k^{(0)}}} \tag{38}$$

1.6 Example: A molecule in a static electric field

Let's apply what we've derived to the example of a molecule in a static electric field. The perturbed Hamiltonian is given by:

$$\hat{H} = \hat{H}^{(0)} + \underline{\xi} \cdot \underline{\hat{\mu}} \tag{39}$$

where $\hat{H}^{(0)}$ is the bare molecular Hamiltonian, $\underline{\xi}$ is the applied static electric field, and $\underline{\hat{\mu}}$ is the molecular dipole operator given by

$$\underline{\hat{\mu}} = \sum_i q_i \cdot \underline{\hat{r}_i} \tag{40}$$

which describes the spatial distribution of charges in the molecule. Note that here we use hats to represent quantum operators and underlined quantities to represent vectors.

The first order response of the ground state energy to the field is simply:

$$E_0^{(1)} = \langle \psi_0^{(0)} | \underline{\xi} \cdot \underline{\hat{\mu}} | \psi_0^{(0)} \rangle = \underline{\xi} \cdot \langle \psi_0^{(0)} | \underline{\hat{\mu}}_0 | \psi_0^{(0)} \rangle \equiv \underline{\xi} \cdot \langle \underline{\hat{\mu}}_0 \rangle \tag{41}$$

where $\langle \underline{\hat{\mu}}_0 \rangle$ is the permanent dipole moment of the molecule in its ground state. This is the first-order Stark shift!

The second order response to the field is

$$E_0^{(2)} = \underline{\xi} \cdot \left(\frac{\sum_{k>0} \underline{\mu}_{0k} \cdot \underline{\mu}_{k0}}{E_0^{(0)} - E_k^{(0)}} \right) \cdot \underline{\xi} \equiv \underline{\xi} \cdot \underline{\underline{\alpha}} \cdot \underline{\xi} \tag{42}$$

where $\underline{\underline{\alpha}}$ is the polarizeability tensor and $\underline{\underline{\alpha}} \cdot \underline{\xi}$ represents an induced dipole moment.

The magnitude of the induced dipole moment depends on (i) whether the molecule has low-lying excited states, which provide small denominators in Eqn. 42, and (ii) the strength of the dipole matrix elements. This second-order behavior is known as the quadratic Stark effect.

2 Degenerate perturbation theory

Above, we examined how perturbation theory may be used to derive first and second-order corrections to the solutions of the zeroth-order Hamiltonian assuming that the eigenfunctions of $\hat{H}^{(0)}$ are unique. However, for many systems, degenerate eigenstates abound. Consider the angular momentum eigenstates of the rigid rotor for instance, which feature degeneracies of $2J + 1$, where J is the angular momentum quantum number. Non-degenerate PT cannot be applied in this case – one needs to do things slightly differently.

Consider a system in which the ground state of the $\hat{H}^{(0)}$ reference Hamiltonian is q-fold degenerate. If the perturbing term $\lambda \hat{H}^{(1)}$ completely lifts this degeneracy then there will be q distinct energy levels. The goal of perturbation theory is to calculate these new energies and the altered wavefunctions associated with the now distinct energy eigenvalues. As before, we can expand the first-order correction to the jth eigenstate in terms of the zeroth-order eigenstates:

$$|\psi_j^{(1)}\rangle = \sum_k c_{kj}^{(1)} |\psi_k^{(0)}\rangle \qquad \text{with} \qquad c_{kj}^{(1)} = \frac{\hat{H}_{kj}^{(1)}}{E_j^{(0)} - E_k^{(0)}} \tag{43}$$

If the ground state is q-fold degenerate, then

$$E_1^{(0)} = E_2^{(0)} = \cdots = E_q^{(0)} \tag{44}$$

and the $\{c_{kj}^{(1)}\}$ are will explode for $j, k \leq q$ as the denominator goes to 0.

How do we get out of this predicament? The idea is to construct a new set of basis functions based on particular linear combinations of our reference $\{|\psi_k^{(0)}\rangle\}$ which diagonalize the $q \times q$ sub-matrix block of $\hat{H}^{(1)}$ with $j, k \leq q$. Once diagonalized, the $\hat{H}_{jk}^{(1)}$ matrix elements with $j \neq k$ are, by definition, zero. The corresponding $\{c_{kj}^{(1)}\}$ coefficients will therefore vanish as the numerator goes to zero, solving our exploding coefficients problem. The remainder of the problem may be solved exactly as we treated it in the first-order non-degenerate case.

Let's call $|\bar{\psi}_j\rangle$ the wavefunctions which diagonalize $\hat{H}^{(1)}$ with $j, k \leq q$. We can generate $|\bar{\psi}_j\rangle$ as linear combinations of the zeroth-order eigenfunctions:

$$|\bar{\psi}_j\rangle = \sum_i^q a_{ji}|\psi_i^{(0)}\rangle \tag{45}$$

Assuming that all other $\hat{H}^{(0)}$ eigenstates are non-degenerate, our reference basis is now given by:

$$\{|\bar{\psi}_1\rangle, |\bar{\psi}_2\rangle, \cdots, |\bar{\psi}_q\rangle, |\psi_{q+1}^{(0)}\rangle, |\psi_{q+2}^{(0)}\rangle, \cdots\} \tag{46}$$

Conveniently, the diagonal elements of the $q \times q$ submatrix of $\hat{H}^{(1)}$ are exactly the first-order energy corrections $E_j^{(1)}$ for $j \leq q$:

$$E_j^{(1)} = \langle\bar{\psi}_j|\hat{H}^{(1)}|\bar{\psi}_j\rangle = \hat{H}_{jj}^{(1)} \quad (j \leq q) \tag{47}$$

For now, we will just emphasize this conceptual approach and won't go into further detail regarding how one actually goes about diagonalizing the blocks of $\hat{H}^{(1)}$ spanned by degenerate $|\psi_j^{(}0)\rangle$ eigenstates.

Note that while we unfortunately have to diagonalize *parts* of $\hat{H}^{(1)}$ in this degenerate case, this is still a much easier job than forgoing perturbation theory entirely and trying to diagonalize the entire thing.