CHM 502 – Module 5 – Time-Independent Perturbation Theory

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Many important problems in quantum mechanics cannot be solved exactly. In these cases, perturbation theory (PT) is an important tool. 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 a Hamiltonian $\hat{H}^{(0)}$ with energy eigenvectors $|\psi_j^{(0)}\rangle$ and eigenvalues $E_j^{(0)}$. We will call this the "reference Hamiltonian" and its eigenvector and eigenvalue solutions the "zeroth-order" solutions (hence their labeling with (0) superscripts).

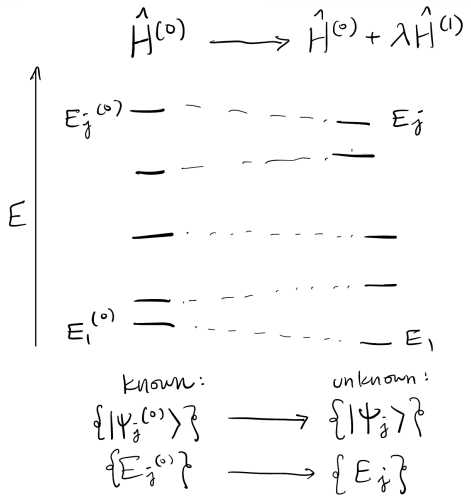
Now consider perturbing this system by adding a "small" perturbation $\hat{H}^{(1)}$:

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

The λ coefficient is just for bookkeeping, as we will see shortly.

We expect that the solutions to $\hat{H}$ – which we will call $|\psi_j\rangle$ and E_j – will not be too different from those of our reference system.

Note: What constitutes a "small" perturbation? The scale for what is considered small is typically set by 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 is to understand how the perturbed system behaves by finding the $|\psi_j\rangle$ and E_j solutions in terms of known quantities. We will attack this problem by first defining expansions for the solutions of $\hat{H}$ 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: our reference Hamiltonian $\hat{H}^{(0)}$, the perturbation $\hat{H}^{(1)}$, and the zeroth-order $E_j^{(0)}$ and $|\psi_j^{(0)}\rangle$. For first-order PT, we truncate the series in Eqns. 3 and 4 at the first power of λ, for second-order PT, we keep terms up to λ^2, and so on and so forth.

Here is a roadmap (and cheat sheet) for how one can find the first few expansion coefficients:

1. Plug in the 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 on either side of Eqn. 5 by powers of λ.

3. Left-project the first-order terms of Eqn. 5 with a zeroth-order 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 Eqn. 6 into first-order terms of Eqn. 5 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

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

6. Then turn to the second-order terms of 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:

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

1.2 Grouping terms in the Schrödinger equation by λ

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

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

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

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

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 the first few powers of λ:

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

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

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

It is 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 zeroth-order eigenvalues and eigenfunctions. The second-order quantities can be expressed in terms of zeroth- and first-order quantities, and so on and so forth.

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:

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

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

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

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

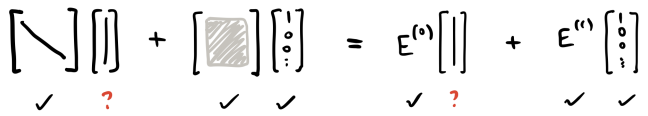
The diagonal elements of $\hat{H}^{(1)}$ therefore directly give us $E_j^{(1)}$, the first-order corrections to the energy eigenvalues. To solve this problem to first order, there is no need to diagonalize $\hat{H}^{(1)}$!

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

1.4 First-order corrections to the energy eigenfunctions

We now consider $|\psi_j^{(1)}\rangle$, the first-order corrections to our energy eigenfunctions. Consider our first-order expression from Eqn. 13. We have found $E_j^{(1)}$ and have just 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 conveniently form a complete, orthonormal basis set); we need only find the expansion coefficients $c_{kj}^{(1)}$:

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

Aside: Before we go further, we must 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 that:

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

Let's use our trusty trick of grouping by powers of λ. All coefficients multiplying factors of λ must evaluate to 0 if we want Eqn. 22 to evaluate to 1 for arbitrary λ:

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

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

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

If $\langle\psi_j^{(0)}|\psi_j^{(1)}\rangle$ is real in Eqn. 24, then $|\psi_j^{(0)}\rangle$ and $|\psi_j^{(1)}\rangle$ must be orthogonal. Without loss of generality, we can choose $\langle\psi_j^{(0)}|\psi_j^{(1)}\rangle$ to be real, and therefore take $c_{jj}^{(1)} = 0$. 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 $\langle\psi_k^{(0)}|$:

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

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

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

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

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

And thus we have found the k^{th} 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 the λ^2 expression from Eqn. 14 and left-project with $\langle\psi_j^{(0)}|$:

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

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

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

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

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

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

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

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

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 unperturbed molecular Hamiltonian, $\underline{\xi}$ is the applied static electric field (which one might take to be oriented along the lab-frame z axis), and $\underline{\hat{\mu}}$ is the dipole operator. Note that here we use hats to represent quantum operators and underlined quantities to represent vectors.

For reference, the dipole operator describes the spatial distribution of charges in the molecule and is given by:

$$\underline{\hat{\mu}} = \sum_j q_j \cdot \underline{\hat{r}}_j \tag{40}$$

which where q_j is the charge and $\underline{\hat{r}}_j$ is the position vector of the j^{th} electron (or nucleus).

The first-order response of the molecule's ground state energy to the field is:

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

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 dependence of the ground state energy on the field is given by:

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

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 (a) whether the molecule has low-lying excited states, which provide small denominators in Eqn. 42, and (b) the magnitude of the matrix elements of the dipole operator. This second-order behavior is known as the quadratic Stark effect.

2 Degenerate perturbation theory

In all of the math above, we assumed that the eigenfunctions of $\hat{H}^{(0)}$ had unique energy eigenvalues. However, degenerate eigenstates abound in many systems. Consider the angular momentum eigenstates of the rigid rotor for instance, which feature degeneracies of $2J+1$. One needs to do things slightly differently in this case.

Consider a system in which the ground state of $\hat{H}^{(0)}$ is q-fold degenerate. If the perturbation $\lambda\hat{H}^{(1)}$ completely lifts this degeneracy then q distinct energy levels will result. The goal of PT 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 j^{th} eigenstate in terms of the zeroth-order eigenstates:

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

If the ground state is q-fold degenerate, then

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

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

To get out of this predicament, we must construct a new basis from particular linear combinations of the degenerate zeroth-order $|\psi_k^{(0)}\rangle$ eigenstates which diagonalize the $q \times q$ block of $\hat{H}^{(1)}$ with $j,k \leq q$. Once diagonalized, the off-diagonal $H_{jk}^{(1)}$ matrix elements with $j \neq k$ are, by definition, zero. The formerly problematic $c_{kj}^{(1)}$ coefficients will now feature a numerator that goes to zero, killing the explosion-causing denominator. 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 the block of $\hat{H}^{(1)}$ with $j,k \leq q$. We 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:

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

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

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

We just emphasize this conceptual approach here and won't go into further detail. 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 and diagonalizing the entire thing.