B7.3 Further Quantum Theory Lecture 9

In practice, it is very unusual to be able to explicitly solve for the stationary states/energy levels of a quantum system (specifically those with infinite-dimensional Hilbert spaces). For this reason, it is essential to have an array of approximate methods to treat more general systems than those you've encountered thus far.

Our first consideration in this direction will be the analysis of systems whose Hamiltonians are "small perturbations" of some reference Hamiltonian (which we imagine we have previously understood):

$$H = H_0 + H'$$

H: total Hamiltonian; H_0: "unperturbed" reference Hamiltonian; H': perturbation

We want to think of H' as being a small perturbation to H_0. To make this clear, we introduce a formal small parameter u controlling the perturbation

$$H = H_0 + uH'$$

Our task is then to develop the eigenstates/eigenvalues of H_u as formal power series in u:

$$H_u \psi_u = E_u \psi_u$$

where $\psi_u = \psi + u\psi' + u^2\psi'' + \dots$ and $E_u = E + uE' + u^2E'' + \dots$. We can choose a normalization for ψ_u relative to ψ as a formal series in u:

$$\langle \psi_u | \psi \rangle = 1$$

Amounts to orthogonality of each $\psi^{(n)}$ $(n \geq 1)$ with ψ: $\langle \psi | \psi \rangle = 1$, $\langle \psi' | \psi \rangle = 0$, $\langle \psi'' | \psi \rangle = 0$, etc., can accomplish this by shifting ψ_u by $u^n \psi_u$ for appropriate n.

(Note that with this normalization, we have $\langle \psi_u | \psi_u \rangle = 1 + O(u^2)$, so going to higher orders will need to normalize.)

Plugging expansions into time-independent Schrödinger equation, get conditions order-by-order in u:

$$(H_0 + uH')\left(\psi + u\psi' + u^2\psi'' + \dots\right) = (E + uE' + u^2E'' + \dots)\left(\psi + u\psi' + u^2\psi'' + \dots\right)$$

Collecting low-order terms:

$O(u^0)$: $H_0\psi = E\psi$

→ ψ is an eigenstate of the unperturbed Hamiltonian with unperturbed energy E.

$O(u^1)$: $H'\psi + H_0\psi' = E'\psi + E\psi'$

→ Reorganizing, $\boxed{(H_0 - E)\psi' = -(H' - E')\psi}$ ✳

$O(u^2)$: $H'\psi' + H_0\psi'' = E''\psi + E'\psi' + E\psi''$

→ $(H_0 - E)\psi'' = -(H' - E')\psi' + E''\psi$

...

To solve (*), we might naively want to write

$$\psi' \stackrel{?}{=} \frac{-1}{H_0 - E} \cdot (H' - E')\psi$$

However, $H_0 - E_0$ is surely not an invertible operator due to the nontrivial kernel. It turns out we can evade this problem. Let's first see how we can solve (*) in a low-brow fashion. We take the following set-up for now:

- $\{\psi_n\}_{n\in I}$ form orthonormal basis of H_0 eigenstates w/ energies $\{E_n\}$.
- Unperturbed $\psi = \psi_k$ for some $k \in I$ where E_k is a non-degenerate energy level, and we have

$$\psi_u = \psi_{k,u} = \psi_k + u\psi_k' + \dots \qquad E_u = E_{k,u} = E_k + uE_k' + \dots$$

First we take the inner product of equation (*) with ψ_k:

$$\langle \psi_k | H_0 - E_k | \psi_k' \rangle = -\langle \psi_k | H' - E_k' | \psi_k \rangle$$
$$0 = -\mathbb{E}_{\psi_k}(H') + E_k'$$
$$E_k' = \mathbb{E}_{\psi_k}(H')$$

Don't even need ψ_k' to get first energy correction; often very useful! Continuing to the corrected state, we consider the expansion in the orthonormal basis:

$$|\psi_k'\rangle = \sum_{n\in I} c_n |\psi_n\rangle \quad \text{w/ } c_n = \frac{\langle \psi_n | \psi_k' \rangle}{\|\psi_n\|} = \langle \psi_n | \psi_k' \rangle$$

Now taking inner product of (*) with ψ_n, we find

$$\langle \psi_n | H_0 - E_k | \psi_k' \rangle = -\langle \psi_n | H' - E' | \psi_k \rangle$$
$$(E_n - E_k)\, c_n = -\langle \psi_n | H' | \psi_k \rangle + E' \delta_{n,k}$$

For $n = k$, LHS & RHS vanish identically (by our choice of E_k'), so c_k unfixed. We set it to zero by our normalization convention. Other coefficients given by

$$c_n = \frac{\langle \psi_n | H' | \psi_k \rangle}{E_k - E_n} \quad ; \; n \neq k$$

Interestingly, we can rewrite this as follows:

$$|\psi_k'\rangle = \left(\sum_{n\neq k} \frac{|\psi_n\rangle\langle\psi_n|}{E_k - E_n} \right) H' |\psi_k\rangle$$

(projection onto orthogonal complement to space spanned by ψ_k)

$$= \left(\sum_{k} \frac{|\psi_k\rangle\langle\psi_k|}{E_k - H_0} \right) (\mathbb{1} - |\psi_k\rangle\langle\psi_k|) H' |\psi_k\rangle$$

$$= \left(\frac{-1}{H_0 - E_k} \right) (H' - E_k') |\psi_k\rangle$$

Before proceeding to examples or higher-order analysis, we should stop and interrogate the idea that H' should be "small". What does it mean? Do these calculations mean anything?

In the finite-dimensional case, this is a (relatively) straightforward exercise, but in the functional analytic setting is quite subtle.

> **Thm. (Kato):** If there exist real constants $a, b \geq 0$ s.t. $\forall \Psi \in \text{Domain}(\mathcal{H})$,
>
> $$\| H'\Psi \| \leq a\|\Psi\| + b\|H_0\Psi\|$$
>
> Then the formal expansions for $\Psi_{u,k}$ & $E_{u,k}$ have finite radius of convergence (estimation takes more effort).

For $\dim(\mathcal{H}) < \infty$, can always find such an a, b. In infinite dimensions, often cannot (including many of the most interesting cases!). Even then, it is often useful to use perturbation theory, interpreted as an asymptotic series.

Example #1: Anharmonic Oscillator

Consider 1-d harmonic oscillator perturbed by "anharmonic" X^4 term.

$$H = \underbrace{\frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2}_{H_0} + u\underbrace{\frac{m^2\omega^3}{\hbar}X^4}_{H'}$$

Define $X = \sqrt{\frac{\hbar}{2m\omega}}(\alpha_+ + \alpha_-)$ and $P = i\sqrt{\frac{\hbar m\omega}{2}}(\alpha_+ - \alpha_-)$ where $[\alpha_-, \alpha_+] = 1$.
Recall unperturbed system has stationary states $|n\rangle$ where $E_n = \hbar\omega(n+\frac{1}{2})$ and $|n\rangle = \frac{\alpha_+^n}{\sqrt{n!}}|0\rangle$ and $\alpha_-|0\rangle = 0$

To compute correction to ground state energy, we need to determine

$$E_0' = \frac{u^2\omega^3}{\hbar}\langle 0|X^4|0\rangle$$
$$= \frac{1}{4}\hbar\omega\,\langle 0|(\alpha_+ + \alpha_-)^4|0\rangle$$

Expanding 4^{th} power of X and remembering to discard terms that clearly give zero, we have

$$E_0' = \frac{1}{4}\hbar\omega\langle 0|\alpha_-\alpha_+\alpha_-\alpha_+ + \alpha_-^2\alpha_+^2|0\rangle = \frac{3}{4}\hbar\omega > 0$$

The perturbed state is $|0'\rangle = \frac{1}{4}\hbar\omega\sum_{n\neq 0}\frac{\langle n|X^4|0\rangle}{-n\hbar\omega} = \frac{-1}{4}\hbar\omega\sum_{n=2,4}\frac{\langle n|X^4|0\rangle}{n\hbar\omega}$

$$= \left[\frac{-1}{16}\langle 4|X^4|0\rangle\right]|4\rangle + \left[\frac{-1}{8}\langle 2|X^4|0\rangle\right]|2\rangle$$

$$= \frac{-\sqrt{4!}}{16}|4\rangle - \frac{6\sqrt{2}}{8}|2\rangle$$

$$= -\sqrt{\frac{3}{32}}|4\rangle - \sqrt{\frac{18}{16}}|2\rangle$$

A lot of fun combinatorics with ladder operators here!

Example #2: Helium atom

Consider two electrons bound to a nucleus of charge $Z = 2$. The Hamiltonian (ignoring more subtle effects) is given by

$$H_{2\text{-electron}} = \underbrace{\left(\frac{|p_1|^2}{2m} - \frac{2e^2}{4\pi\epsilon_0|x_1|^2}\right)}_{H_1} + \underbrace{\left(\frac{|p_2|^2}{2m} - \frac{2e^2}{4\pi\epsilon_0|x_2|^2}\right)}_{H_2} + \underbrace{\frac{e^2}{4\pi\epsilon_0|x_1 - x_2|^2}}_{H_{int}}$$

The unperturbed stationary states are just antisymmetrized tensor products of Hydrogenic stationary states (with $Z = 2$), a.k.a, the Hartree approximation.

$$\psi^{m_{s,1}, m_{s,2}}_{\{n_1,\ell_1,m_1\},\{n_2,\ell_2,m_2\}} = \psi^{m_1}_{n_1,\ell_1}(r_1)\,\psi^{m_2}_{n_2,\ell_2}(r_2)\,\mathcal{C}\,|m_{s,1}, m_{s,2}\rangle$$

($m_{s,1}$: $\pm 1/2$, $m_{s,2}$: $\pm 1/2$)

This is a highly degenerate system, but the ground state is unique.

$$\psi_0 = \psi^0_{1,0}(r_1)\,\psi^0_{1,0}(r_2)\,\mathcal{C}\left(\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{2}\right)$$

$$\psi^0_{1,0}(r) = \left(\frac{8}{\pi a^3}\right)^{1/2}\exp\left(\frac{-2r}{a}\right)$$

$$E_0 = \frac{-2Ze^2}{4\pi\epsilon_0 a} = \frac{-4e^2}{4\pi\epsilon_0 a}$$

We can compute the "first order" correction to this ground state energy:

$$E_0' = \langle\psi_0|H_{int}|\psi_0\rangle = \frac{e^2}{4\pi\epsilon_0}\,\mathbb{E}_{\psi_0}\left(\frac{1}{|x_1 - x_2|^2}\right)$$

$$= \left(\frac{8}{\pi a^3}\right)^2\left(\frac{e^2}{4\pi\epsilon_0}\right)\int d^3r_1\,d^3r_2\,\frac{\exp\left(\frac{-2}{a}(r_1 + r_2)\right)}{|r_1 - r_2|}$$

$$= \frac{2e^2}{\pi^2 a\,\epsilon_0}\int d^3r_1\,d^3r_2\,\frac{e^{-(r_1+r_2)}}{|r_1 - r_2|} \qquad \text{(simplify by spherical symmetry)}$$

$$= \frac{2e^2}{\pi^2 a\,\epsilon_0}\int (4\pi r_2^2)(2\pi r_1\sin\theta_1)\frac{e^{-(r_1+r_2)}}{(r_1^2 + r_2^2 - 2r_1r_2\cos\theta_1)^{1/2}}\,dr_1\,dr_2\,d\theta_1$$

$$= \frac{16e^2}{a\,\epsilon_0}\int dr_1\,dr_2\,\exp(-r_1 - r_2)\int\frac{\sin\theta\,d\theta}{(r_1^2 + r_2^2 - 2r_1r_2\cos\theta)^{1/2}}$$

$$= \frac{5}{16}\left(\frac{4e^2}{4\pi\epsilon_0 a}\right)$$

So $\left|\frac{E_0'}{E_0}\right| = \frac{5}{16} = .3125$, not exactly a small correction, but for reference:

$$E_0 + E_0' \approx -0.69\left(\frac{e^2}{\pi\epsilon_0 a}\right), \quad E_0 \approx -1\cdot\left(\frac{e^2}{\pi\epsilon_0 a}\right), \quad E_{exp} \approx -0.73\left(\frac{e^2}{\pi\epsilon_0 a}\right)$$

Not bad, actually! From a rigorous perspective, this expansion is probably divergent; in terms of Z, one can establish convergence for $Z > 7.7$ (rather than $Z = 2$).

There is a small modification to make in the case of degenerate energy levels. As before, we need (from $*$) that $RHS \in Ran(H_0 - E)$. To generalize the construction from before, we prove the following:

Lemma: $Ran(H_0 - E) = \left(Ker(H_0 - E)\right)^{\perp}$

Proof: We prove double inclusion.

- $Ran(H_0-E) \subseteq \left(Ker(H_0-E)\right)^{\perp}$: let $\omega \in Ran(H_0-E)$, so $\omega = (H_0-E)\tilde{\omega}$ for some $\tilde{\omega} \in \mathcal{H}$. Now $\forall v \in Ker(H_0-E)$, $\langle v|\omega\rangle = \langle v|H_0-E|\tilde{\omega}\rangle = \langle (H_0-E)v|\tilde{\omega}\rangle = 0$

- $\left(Ker(H_0-E)\right)^{\perp} \subseteq Ran(H_0-E) \overset{(*)}{\iff} \left(Ran(H_0-E)\right)^{\perp} \subseteq Ker(H_0-E)$. Let $\omega \in \left(Ran(H_0-E)\right)^{\perp}$ and $v \in \mathcal{H}$. Then $0 = \langle (H_0-E)v|\omega\rangle = \langle v|(H_0-E)\omega\rangle \ \forall\, v$, so $(H_0-E)\omega \equiv 0$. ▩

(*) In ∞-dim'l space, need here that $H_0 - E$ is a closed operator, which is true for self-adjoint operators

Thus we need $(H'-E')\Psi \in \left(Ker(H_0-E)\right)^{\perp}$. Let $\{\Phi_r\}_{r\in I}$ be orthonormal basis for H_0 eigenspace w/eigenvalue E, so basis for $Ker(H_0-E)$.

Thus $\Psi = \sum c_r \Phi_r$, where we require $\sum c_r \langle \Phi_s|H'-E'|\Phi_r\rangle = 0 \ \forall s \in I$, i.e., Ψ must be an eigenvector of the matrix $\langle \Phi_s|H'|\Phi_r\rangle$ with eigenvalue E'.

Solving for Ψ' then proceed as in non-degenerate case, but now some ambiguities remain:

$$|\Psi_K'\rangle = \sum_{E_n \neq E_K} \left(\frac{\langle \Psi_n|H'|\Psi_K\rangle}{E_K - E_n}\right)|\Psi_n\rangle + \sum_{\substack{E_r = E_K \\ \Phi_r \perp \Psi_K}} \lambda_r \Phi_r$$

(free coefficients at this order)

Slogan

In case of degeneracy, must choose basis for unperturbed states that diagonalizes perturbation restricted to degenerate subspaces. In this basis, formulae from non-degenerate P.T. apply, plus ambiguity.