B7.3 Further Quantum Theory Lecture 10

We have from last lecture the equations of first-order, non-degenerate perturbation theory:

$$(H_0 - E)\Psi' = (E' - H')\Psi \quad \begin{cases} \triangleright\ E_k' = \langle \Psi_k | H' | \Psi_k \rangle \\ \triangleright\ \Psi_k' = \sum_{n \neq k} \left(\frac{\langle \Psi_n | H' | \Psi_k \rangle}{E_k - E_n} \right) |\Psi_n\rangle \end{cases}$$

Let's look at this in another case involving more integration than last time.

Example #2: Helium atom

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

$$H_{2\text{-electron}} = \underbrace{\left(\frac{|P_1|^2}{2m} - \frac{2e^2}{|x_1|} \right)}_{H_1} + \underbrace{\left(\frac{|P_2|^2}{2m} - \frac{2e^2}{|x_2|} \right)}_{H_2} + \underbrace{\frac{e^2}{|\underline{x}_1 - \underline{x}_2|}}_{H_{int}}$$

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

$$\Psi^{m_{s,1}, m_{s,2}}_{\{n_1, l_1, m_1\}, \{n_2, l_2, m_2\}} = \Psi^{m_1}_{n_1, l_1}(\underline{r}_1) \Psi^{m_2}_{n_2, l_2}(\underline{r}_2) \otimes |\underbrace{m_{s,1}}_{\pm 1/2}, \underbrace{m_{s,2}}_{\pm 1/2}\rangle$$

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

$$\Psi_0 = \Psi^0_{1,0}(\underline{r}_1) \Psi^0_{1,0}(\underline{r}_2) \otimes \left(\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{2} \right)$$

$$\left(\frac{8}{\pi a^3}\right)^{1/2} \exp\left(\frac{-2r_i}{a}\right)$$

$$E_0 = \frac{-2Z^2 e^2}{2a} = \frac{-4e^2}{a}$$

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

$$E_0' = \langle \Psi_0 | H_{int} | \Psi_0 \rangle = e^2 \mathbb{E}_{\Psi_0}\left(\frac{1}{|\underline{x}_1 - \underline{x}_2|} \right)$$

$$= \left(\frac{8e}{\pi a^3} \right)^2 \int d^3 r_1 d^3 r_2 \frac{\exp\left(-\frac{4}{a}(r_1 + r_2)\right)}{|\underline{r}_1 - \underline{r}_2|}$$

$$= \frac{e^2}{16\pi^2 a} \int d^3 r_1 d^3 r_2 \frac{e^{-(r_1 + r_2)}}{|\underline{r}_1 - \underline{r}_2|} \qquad \text{(simplify by spherical symmetry)}$$

$$= \frac{e^2}{16\pi^2 a} \int (4\pi r_2^2)(2\pi r_1^2 \sin\theta_1) \frac{e^{-(r_1 + r_2)}}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_1)^{1/2}} dr_1\, d\theta_1\, dr_2$$

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

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

Example #2 (cont'd):

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

$$E_0 + E_0' \approx -0.69\left(\frac{4e^2}{a}\right), \quad E_0 \approx -1\cdot\left(\frac{4e^2}{a}\right), \quad E_{exp} \approx -0.73\left(\frac{4e^2}{a}\right)$$

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 $\in \mathrm{Ran}(H_0 - E)$. To generalize the construction from before, we prove the following, which clarifies non-deg. case as well.

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

Proof: We prove double inclusion.

- $\mathrm{Ran}(H_0 - E) \subseteq \left(\mathrm{Ker}(H_0-E)\right)^{\perp}$: let $\omega \in \mathrm{Ran}(H_0 - E)$, so $\omega = (H_0 - E)\tilde{\omega}$ for some $\tilde{\omega} \in \mathcal{H}$. Now $\forall v \in \mathrm{Ker}(H_0 - E)$, $\langle v | \omega \rangle = \langle v | H_0 - E | \tilde{\omega}\rangle = \langle (H_0 - E) v | \tilde{\omega}\rangle = 0$
- $\left(\mathrm{Ker}(H_0-E)\right)^{\perp} \subseteq \mathrm{Ran}(H_0 - E) \overset{\star}{\iff} \left(\mathrm{Ran}(H_0-E)\right)^{\perp} \subseteq \mathrm{Ker}(H_0 - E)$. Let $\omega \in \left(\mathrm{Ran}(H_0 - E)\right)^{\perp}$ 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 $(H' - E')\Psi \in \left(\mathrm{Ker}(H_0 - E)\right)^{\perp}$. Let $\{\phi_r\}_{r\in I}$ be orthonormal basis for H_0 eigenspace w/ eigenvalue E, so basis for $\mathrm{Ker}(H_0 - E)$ and $\Psi = \sum c_r \phi_r$.

We now need to require $\sum_r c_r \langle \phi_s | H' - E' | \phi_r \rangle = 0$ $\forall s \in I$, i.e., $\begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$ must be an eigenvector of the matrix $\langle \phi_s | H' | \phi_r\rangle$ with eigenvalue E'.

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.

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

Ambiguities will be fixed at higher order, don't effect analysis at first order.

Example #3: Spin-Orbit coupling

The "fine structure" of Hydrogen arises from a number of corrections to the Hydrogen Hamiltonian due to relativistic effects.

- $H'_{KE} = \frac{-P^4}{8m^3c^2}$
- $H'_{SO} = \frac{e^2}{2m^2c^2}\frac{\underline{L}\cdot\underline{S}}{r^3}$
- $H'_{Darwin} = \frac{\pi\hbar^2 e^2}{2mc^2}\delta^3(\underline{r})$

We'll focus on the spin-orbit interaction for now. Note $(\underline{L}\cdot\underline{S}) = \frac{1}{2}(J^2 - L^2 - S^2)$ where $\underline{J} = \underline{L} + \underline{S}$.
Thus we're interested in

$$\langle \Psi^{m'}_{n',\ell',j'} | H'_{SO} | \Psi^{m}_{n,\ell,j} \rangle = \delta_{\ell\ell'}\delta_{jj'}\delta_{m,m'}\frac{e^2}{2m^2c^2}\frac{\hbar^2}{2}\left\{ j(j+1) - \ell(\ell+1) - \frac{3}{4} \right\} \cdot \int_0^\infty r^2 dr \frac{S_{n',\ell'}(r) S_{n,\ell}(r)}{r^3}$$

for fixed n, H'_{SO} is diagonalized in the added-spin basis. There are tricks to evaluate this integral (see 5.3 of Sakurai); we will just quote

$$\left\langle \frac{1}{r^3} \right\rangle_{n,\ell} = \frac{1}{a^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)}$$

From which we deduce the first energy corrections

$$E'_n = \frac{e^4}{4m^2c^2a^2}\left(\frac{j(j+1) - \ell(\ell+1) - 3/4}{n^3 \ell(\ell+1/2)(\ell+1)} \right)$$

$$= \frac{E_n^2 n}{mc^2}\left(\frac{j(j+1) - \ell(\ell+1) - 3/4}{\ell(\ell+1/2)(\ell+1)} \right)$$

$$= \frac{E_n^2 n}{mc^2}\begin{cases} \ell & \text{if } j = \ell + 1/2 \\ -(1+\ell) & \text{if } j = \ell - 1/2 \end{cases}$$

need to restrict to $\ell = 0$. Amazingly, this turns out to be the right answer including $\ell = 0$ after including the Darwin term.

So there is a splitting between different j-values at fixed ℓ. However, Kinetic correction and Darwin term contribute at some order of magnitude, so need to treat all three. Result is rather surprising! Dependance on ℓ cancels out and only splitting of energy levels is for different values of j.

This can be understood if we use a relativistic treatment via the Dirac equation.

Second order (non-degenerate) P.T.: Now we need to solve for E_k'', ψ_k'':

$$(H_0 - E_k)\psi_k'' = (E_k' - H')\psi_k' + E_k''\psi_k$$

As before, we should arrange E_k'' so R.H.S. is orthogonal to ψ_k, then "invert" $H_0 - E_k$:

$$\langle\psi_k|H_0 - E_k|\psi_k''\rangle = \langle\psi_k|E_k' - H'|\psi_k'\rangle + \langle\psi_k|E_k''|\psi_k\rangle$$

$$0 = -\langle\psi_k|H'|\psi_k'\rangle + E_k''$$

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

What about ψ_k''?

$$\psi_k'' = (H_0 - E_k)^{-1}\cdot\left((E_k' - H')\psi_k' + E''\psi_k\right)$$

$$= \sum_{\substack{m\neq k\\ n\neq k}}\frac{|\psi_m\rangle\langle\psi_m|E_k' - H'|\psi_n\rangle\langle\psi_n|H'|\psi_k\rangle}{(E_m - E_k)(E_k - E_n)}$$

$$= \sum_{\substack{m\neq k\\ n\neq k}}\frac{|\psi_m\rangle\langle\psi_m|H'|\psi_n\rangle\langle\psi_n|H'|\psi_k\rangle}{(E_m - E_k)(E_n - E_k)} - \sum_{m\neq k}\frac{|\psi_m\rangle\langle\psi_m|H'|\psi_k\rangle\langle\psi_k|H'|\psi_k\rangle}{(E_m - E_k)^2}$$

Note, though, that now $\|\psi_k + u\psi_k' + u^2\psi_k''\|^2 = 1 + u^2\|\psi_k'\|^2 + \mathcal{O}(u^3)$, so to normalize to order u^2, we need to divide by $(1 + u^2\|\psi_k'\|^2)^{-1/2} \approx 1 - \frac{1}{2}u^2\|\psi_k'\|^2$. The correction term multiplies ψ_k to give an additional $O(u^2)$ correction:

$$|\tilde{\psi}_k''\rangle = |\psi_k''\rangle - \frac{1}{2}\sum_{m\neq k}\frac{|\psi_k\rangle\langle\psi_k|H'|\psi_m\rangle\langle\psi_m|H'|\psi_k\rangle}{(E_m - E_k)^2}$$

(re-normalized correction to ψ_k)

There is a neat trick to go to higher orders. Consider $H_u\psi_u = E_u\psi_u$ & $H_v\psi_v = E_v\psi_v$ for u,v independant formal variables. Then we have

$$\left.\begin{aligned}\langle\psi_u|H_u - H_v|\psi_v\rangle &= (u-v)\langle\psi_u|H'|\psi_v\rangle \\ &= (E_u - E_v)\langle\psi_u|\psi_v\rangle\end{aligned}\right\} \quad \frac{E_u - E_v}{u-v} = \frac{\langle\psi_u|H'|\psi_v\rangle}{\langle\psi_u|\psi_v\rangle}$$

$$\frac{E_u - E_v}{u-v} = \sum_{n=1}^{\infty}\frac{u^n - v^n}{u-v}E^{(n)} = \sum_{n=1}^{\infty}\sum_{k=0}^{n-1}u^k v^{n-1-k}E^{(n)}$$

$$\frac{\langle\psi_u|H'|\psi_v\rangle}{\langle\psi_u|\psi_v\rangle} = \frac{\langle\psi|H'|\psi\rangle + u\langle\psi'|H'|\psi\rangle + v\langle\psi|H'|\psi'\rangle + u^2\langle\psi''|H'|\psi\rangle + uv\langle\psi'|H'|\psi'\rangle + \cdots}{1 + uv\langle\psi'|\psi'\rangle + u^2v\langle\psi''|\psi'\rangle + uv^2\langle\psi'|\psi''\rangle + \cdots}$$

Now any term of the form $u^a v^b$ with $a+b+1=n$ computes $E^{(n)}$.

- $E^{(1)} = \langle\psi|H'|\psi\rangle$
- $E^{(2)} = \langle\psi'|H'|\psi\rangle = \langle\psi|H'|\psi'\rangle$
- $E^{(3)} = \langle\psi''|H'|\psi\rangle = \langle\psi'|H'|\psi'\rangle - \langle\psi'|\psi'\rangle = \langle\psi|H'|\psi''\rangle$

etc.

So immediately, $$E_k''' = \sum_{m,n\neq k}\frac{\langle\psi_k|H'|\psi_m\rangle\langle\psi_m|H'|\psi_n\rangle\langle\psi_n|H'|\psi_k\rangle}{(E_k - E_m)(E_k - E_n)} - \sum_{m\neq k}\frac{\langle\psi_k|H'|\psi_m\rangle\langle\psi_m|H'|\psi_k\rangle}{(E_k - E_m)^2}$$

Hopefully you'll never have to compute a third-order correction to any energy-levels!