B7.3 Further Quantum Theory Lecture 11

Finishing up perturbation theory, let's take a look at higher orders. Recall our expansion of the time-independent Schrödinger equation:

$$H_0 \psi_n = E_n \psi_n$$

$$(H_0 - E_n)\psi_n' = -(H' - E_n')\psi_n$$

$$(H_0 - E_n)\psi_n'' = -(H' - E_n')\psi_n' + E_n''\psi_n$$

We need to solve the last equation for E_n'' and ψ_n''. As previously, we choose E_n'' so that the RHS is in the range of $(H_0 - E_n)$, i.e., in the complement of the kernel of $(H_0 - E_n)$. In our non-degenerate case, that means the RHS is orthogonal to ψ_n:

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

$$= -\langle \psi_k | H' | \psi_k' \rangle + E_k'' \qquad (\psi_n \perp \psi_n' \text{ by normalization})$$

$$E_k'' = \langle \psi_n | H' | \psi_n' \rangle$$

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

$$= \sum_{n \neq k} \frac{|\langle \psi_n | H' | \psi_n \rangle|^2}{E_n - E_n}$$

Observe that if ψ_n is the ground state (so $E_n = E_0$), then $(E_n - E_n) < 0$, and $E_0'' \leq 0$ (always corrected down).

What about ψ_k''?

$$\psi_k'' = (H_0 - E_n)^{-1} \cdot \left((E_{n'} - H')\psi_n' + E''\psi_n \right)$$

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

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

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

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

renormalized so $\| \psi_n + u\psi_n' + u^2 \tilde{\psi}_n'' \|^2 = 1 + O(u^3)$

We're not obligated to renormalize like this, but it is a warning we need to be attentive to normalizations at high orders.

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 independent formal variables. Then we have

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

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

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

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!

When no small parameters are present, there are still useful techniques for estimating stationary-state energy levels. An important class of techniques go by the name of "variational methods".

<u>Def</u>: The Rayleigh quotient associated to a self-adjoint operator A and a vector $\Psi \in \mathcal{H}$ is the expectation value

$$\mathcal{F}_A(\Psi) = \mathbb{E}_\Psi(A) = \frac{\langle\psi|A|\psi\rangle}{\langle\psi|\psi\rangle}.$$

As is suggested by the notation, for fixed A this gives a function on $\mathcal{H}$ (and in fact on $\mathbb{P}(\mathcal{H})$). Now we have an important result.

<u>Prop</u>: The stationary points of $\mathcal{F}_A$ are precisely the eigenvectors of A.

<u>Proof</u>: For any vector $\phi \in \mathcal{H}$, take

$$\frac{d}{du}\mathcal{F}_A(\psi+u\phi) = \frac{d}{du}\left\{\frac{\langle\psi+u\phi|A|\psi+u\phi\rangle}{\langle\psi+u\phi|\psi+u\phi\rangle}\right\}$$

$\mathcal{F}_H(\psi)$

$$= \frac{\langle\psi|A|\phi\rangle+\langle\phi|A|\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|A|\psi\rangle}{\langle\psi|\psi\rangle^2}\Big(\langle\phi|\psi\rangle+\langle\psi|\phi\rangle\Big)$$

$$= \frac{\langle\psi|A-\mathcal{F}_H(A)|\phi\rangle+\langle\phi|A-\mathcal{F}_H(A)|\psi\rangle}{\langle\psi|\psi\rangle}$$

$$= \frac{2\mathrm{Re}\big(\langle\phi|A-\mathcal{F}_H(A)|\psi\rangle\big)}{\langle\psi|\psi\rangle} = 0$$

By a parallel computation, $\displaystyle \frac{d}{du}\mathcal{F}_A(\psi+iu\phi) = \frac{2\mathrm{Im}\big(\langle\phi|A-\mathcal{F}_H(A)|\psi\rangle\big)}{\langle\psi|\psi\rangle} = 0$

Thus we conclude that ψ is a stationary vector if and only if: $\langle\phi|A-\mathcal{F}_H(A)|\psi\rangle = 0 \quad \forall \phi\in\mathcal{H}$

This requires $A|\psi\rangle = \mathcal{F}_H(A)|\psi\rangle$ ▨

An immediate generalisation of this proof shows that if we restrict our variations of ψ to lie in a subspace $K \subseteq \mathcal{H}$, then stationary vectors are those for which $(A-\mathcal{F}_A(\psi))|\psi\rangle \in K^\perp$. The original proof above is the case $K=\mathcal{H}$.

There are a few ways to take advantage of this. First we will exploit the stationary property of energy eigenstates to prove the quantum virial theorem.

Thm: Let $H = \underbrace{\frac{|\underline{P}|^2}{2m}}_{T} + \underbrace{V(\underline{x})}_{V}$. Then in an energy eigenstate ψ of energy E, one has

$$2\,\mathbb{E}_\psi(T) - \mathbb{E}_\psi(\underline{x}\cdot\underline{\nabla}V) = 0$$

Proof: Consider the 1-parameter family of states $\psi_\lambda(\underline{x}) = \lambda^{3/2}\psi(\lambda\underline{x})$. Stationarity of the Rayleigh quotient $\mathcal{F}_H(\psi_\lambda)$ at $\lambda = 1$ implies:

$$0 = \frac{d}{d\lambda}\left(\mathbb{E}_{\psi_\lambda}(T) + \mathbb{E}_{\psi_\lambda}(V)\right)\Big|_{\lambda=1}$$

$$\begin{aligned}\mathbb{E}_{\psi_\lambda}(T) &= \int d^3\underline{x}\,\lambda^3\,\overline{\psi}(\lambda\underline{x})\left(\frac{-\hbar^2}{2m}\nabla^2\right)\psi(\lambda\underline{x})\\ &= \int d^3\underline{x}'\,\overline{\psi}(\underline{x}')\left(\frac{-\hbar^2}{2m}\lambda^2(\nabla')^2\right)\psi(\underline{x}')\\ &= \lambda^2\,\mathbb{E}_\psi(T)\end{aligned}$$

$$\frac{d}{d\lambda}\mathbb{E}_{\psi_\lambda}(T)\Big|_{\lambda=1} = 2\,\mathbb{E}_\psi(T)$$

$$\begin{aligned}\mathbb{E}_{\psi_\lambda}(V) &= \int d^3\underline{x}\,\lambda^3\,\overline{\psi}(\lambda\underline{x})V(\underline{x})\psi(\lambda\underline{x})\\ &= \int d^3\underline{x}'\,\overline{\psi}(\underline{x}')V(\lambda^{-1}\underline{x}')\psi(\underline{x}')\end{aligned}$$

$$\frac{d}{d\lambda}\mathbb{E}_{\psi_\lambda}(V) = \int d^3\underline{x}\,\overline{\psi}(\underline{x})\left(\frac{-1}{\lambda^2}\right)\underline{x}\cdot\underline{\nabla}V(\underline{x})\psi(\underline{x})$$

$$\frac{d}{d\lambda}\mathbb{E}_{\psi_\lambda}(V)\Big|_{\lambda=1} = \mathbb{E}_\psi\left(-\underline{x}\cdot\underline{\nabla}V(\underline{x})\right)$$

$$0 = 2\,\mathbb{E}_\psi(T) - \mathbb{E}_\psi(\underline{x}\cdot\underline{\nabla}V)$$

A particularly simple case is when $V(\underline{x})$ is homogeneous in the coordinates. Suppose $V(\lambda\underline{x}) = \lambda^N V(\underline{x})$. Then we have $\underline{x}\cdot\underline{\nabla}V = NV$, so the virial theorem tells us:

$$2\,\mathbb{E}_\psi(T) - N\,\mathbb{E}_\psi(V) = 0$$

Meanwhile, because ψ is an energy eigenstate, $\mathbb{E}_\psi(T) + \mathbb{E}_\psi(V) = E$. Combining these equations, we get

$$\mathbb{E}_\psi(T) = \frac{NE}{2+N} \qquad \mathbb{E}_\psi(V) = \frac{2E}{2+N}$$

For example, in Harmonic oscillator, $N = 2$, so $\mathbb{E}_\psi(T) = \mathbb{E}_\psi(V) = \frac{E}{2}$. Alternatively, for the Coulomb potential $N = -1$, so $\mathbb{E}_\psi(T) = -E$, $\mathbb{E}_\psi(V) = 2E$.

An important corollary of the stationarity theorem is as follows:

<u>Corollary</u>: If $\mathcal{F}_A(\Psi)$ is bounded below and achieves its lower bound, then $\min_{\mathcal{H}} \mathcal{F}_A$ is the smallest eigenvalue of A (call it a_0). For any $\Psi \in \mathcal{H}$, $\mathcal{F}_A(\Psi) \geq a_0$.

<u>Proof</u>: if minimum is achieved, it is a stationary value, so an eigenvalue. since it is the minimum of $\mathcal{F}_A$, it must be the smallest eigenvalue.

<u>Alternate proof</u>: Let Ψ_n be complete basis of A-eigenstates with $A\Psi_n = a_n \Psi_n$ and $a_0 \leq a_i$ for $i = 1, 2, \dots$
For any $\Psi \in \mathcal{H}$, we have

$$\Psi = \sum_{n=0} c_n \Psi_n \implies \mathcal{F}_A(\Psi) = \frac{\sum a_n |c_n|^2}{\sum |c_n|^2} = \frac{\sum \overbrace{(a_n - a_0)}^{\geq 0} \overbrace{|c_n|^2}^{\geq 0}}{\sum |c_n|^2} + a_0 \geq a_0$$

Most frequently, we are interested in the case $A = H$, where this result allows us to produce upper bounds on the ground state energy.

In practice, this is usually utilized as follows.

- One makes a variational ansatz for the ground state wave function $\Psi_{\text{Ansatz}}(\underline{x}; \lambda_1, \lambda_2, \dots, \lambda_N)$ which is a guess for the form of the wavefunction with some number of free parameters $\lambda_1, \dots, \lambda_N$.
- One then computes as a function of the free parameters $\mathcal{F}_H(\Psi_{\text{ansatz}}) = F(\lambda_1, \dots, \lambda_N)$ and we minimize, imposing $\partial_{\lambda_1} F = \dots = \partial_{\lambda_N} F = 0$. At the minimum, F gives an upper bound on the groundstate energy E_0.
- If the variational ansatz is wisely chosen, one hopes to actually get a good variational estimate of the ground state energy.

As a standard and illustrative example, we consider again the Helium atom.

Example: Variational approach to Helium atom.

Recall the Helium Hamiltonian $H = \frac{|\underline{p}_1|^2}{2m_e} + \frac{|\underline{p}_2|^2}{2m_e} - \frac{2e^2}{|\underline{x}_1|} - \frac{2e^2}{|\underline{x}_2|} + \frac{e^2}{|\underline{x}_1 - \underline{x}_2|}$. We introduce a variational Ansatz for the ground state wavefunction:

$$\Psi_Z(\underline{r}_1, \underline{r}_2) = \left(\frac{Z^3}{\pi a^3}\right) \exp\left(\frac{-Z}{a}(r_1 + r_2)\right)$$

This is the ground state for the non-interacting Hamiltonian $H_Z^{Hartree} = \frac{|\underline{p}_1|^2}{2m_e} + \frac{|\underline{p}_2|^2}{2m_e} - Ze^2\left(\frac{1}{|\underline{x}_1|} + \frac{1}{|\underline{x}_2|}\right)$, with energy eigenvalues

$$H_Z^{Hartree} \Psi_Z(\underline{r}_1, \underline{r}_2) = \frac{-Z^2 e^2}{a} \qquad \left(\text{Bohr radius } a = \frac{\hbar^2}{m_e e^2}\right)$$

The intuition is that some of the effect of the two electrons can be accounted for by saying some of the nuclear charge is "screened", so the electrons should feel $Z < 2$ effectively.

Now we evaluate:

$$\mathcal{F}_H(\Psi_Z) = \underbrace{E_{\Psi_Z}(T)}_{= -E_Z} + \underbrace{E_{\Psi_Z}(V)}_{= \frac{2}{Z} E_{\Psi_Z}(V_Z^{Hartree}) = \frac{2}{Z}(2E_Z)} + \underbrace{E_{\Psi_Z}\left(\frac{e^2}{|\underline{x}_1 - \underline{x}_2|}\right)}_{= \frac{5}{8}\frac{Ze^2}{a}} = \frac{e^2}{a}\left\{Z^2 - 4Z + \frac{5Z}{8}\right\}$$

same calculation as in 1^{st} order perturbation theory

Minimizing, we solve $2Z - 4 + 5/8 = 0 \Rightarrow Z = 2 - \frac{5}{16} = \frac{27}{16}$.

$\frac{5}{16}$ units of charge "screened"

Plugging back in, $\mathcal{F}_H(\Psi_{Z_*}) = \frac{-e^2}{a}\left(\frac{27}{16}\right)^2 \approx 2.85\left(\frac{-e^2}{a}\right)$ (~2.5% error)

Compare: 0^{th} order perturbation theory: $4.00\left(\frac{-e^2}{a}\right)$

1^{st} order perturbation theory: $\frac{-e^2}{a}\left(\frac{22}{8}\right) \approx 2.75\left(\frac{-e^2}{a}\right)$ (~6% error)

Experimental value: $2.92\left(\frac{-e^2}{a}\right)$

Pretty good! Can improve more by introducing more complicated ansatz. A very powerful method when applied with enough skill!