B7.3 Further Quantum Theory Lecture 12

Last time we defined the Rayleigh quotient $\mathcal{F}_A(\psi) = \mathbb{E}_\psi(A)$ as a function of $\psi \in \mathcal{H}$ (or $\mathbb{P}(\mathcal{H})$) and proved that A-eigenstates correspond with stationary points of $\mathcal{F}_A$.

An important corollary of the stationarity theorem is as follows:

Corollary: 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 $\psi \in \mathcal{H}$, $\mathcal{F}_A(\psi) \geq a_0$.

Proof: If minimum is achieved, it must be a stationary value, and therefore an eigenvalue. Since it is the minimum of $\mathcal{F}_A$, and $\mathcal{F}_A$ takes all eigenvalues of A as values, the minimum must be the smallest eigenvalue.

An alternate proof may be illuminating.

Alternate proof: Let ψ_n be complete basis of A-eigenstates with $A\psi_n = a_n\psi_n$ and $a_0 \leq a_i$ for $i = 1, 2, \ldots$
For any $\psi \in \mathcal{H}$, we have

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

($a_n - a_0 \geq 0$, $|c_n|^2 \geq 0$)

The most common case (in quantum theory) is when $A = H$, where this result leads to upper bounds on the ground state energy of a system.

The usual procedure is as follows:

- Make a variational ansatz for the ground state wave-function: $\psi_{\text{Ansatz}}(\underline{x}; \lambda_1, \ldots, \lambda_N)$ which depends on some number (N) of complex parameters $(\lambda_1, \lambda_2, \ldots, \lambda_N)$.
- Compute the Rayleigh quotient $\mathcal{F}_H(\psi_{\text{Ansatz}}) = F(\lambda_1, \ldots, \lambda_N)$ as a function of the $\{\lambda_i\}$.
- Minimize with respect to the parameters: $(\partial_{\lambda_i} F)(\lambda_{1,*}, \lambda_{2,*}, \ldots, \lambda_{N,*}) = 0$. Minimum gives upper bound on ground state energy.

$$E_0 \leq F(\lambda_{1,*}, \lambda_{2,*}, \ldots, \lambda_{N,*})$$

- If ansatz is wisely chosen, one hopes to get not just upper bound but good variational estimate of ground state energy.

The only limit is our own ingenuity/creativity in concocting good variational ansatz.

As a standard and illustrative example, we will reconsider the Helium atom. Recall the Hamiltonian

$$H = \frac{|\underline{p}_1|^2}{2m_e} + \frac{|\underline{p}_2|^2}{2m_e} - 2e^2\left(\frac{1}{|\underline{x}_1|} + \frac{1}{|\underline{x}_2|}\right) + \frac{e^2}{|\underline{x}_1 - \underline{x}_2|}$$

We introduce a physically-motivated **variational Ansatz** for the ground state wavefunction:

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

Why this ansatz? This is the ground state for the "mean field Hamiltonian"

$\frac{-Z^2e^2}{a}$ ↓ (Bohr radius $a = \frac{\hbar^2}{m_e e^2}$)

$$H_Z^{MF} = \frac{|\underline{p}_1|^2}{2m_e} + \frac{|\underline{p}_2|^2}{2m_e} - Ze^2\left(\frac{1}{|\underline{x}_1|} + \frac{1}{|\underline{x}_2|}\right), \qquad H_Z^{MF}\psi_Z = E_Z\psi_Z$$

The physical intuition is that either one of the electrons should feel a reduced total nuclear charge because the other electron will "screen" some of it (and will on average be at the origin). If second electron just sat exactly at the origin could have $Z = 1$. Actually expect $1 < Z < 2$.

Now we need to compute:

$\frac{1}{2m}(|p_1|^2 + |p_2|^2)$ ↓ $\quad -2e^2\left(\frac{1}{|\underline{x}_1|} + \frac{1}{|\underline{x}_2|}\right)$ ↓

$$\mathcal{F}_{II}(\psi_Z) = \mathbb{E}_{\psi_Z}(T) + \mathbb{E}_{\psi_Z}(V) + \mathbb{E}_{\psi_Z}\left(\frac{e^2}{|\underline{x}_1 - \underline{x}_2|}\right)$$

First two terms follow from virial theorem $\left(H_Z^{MF} = T + \frac{Z}{2}V\right)$

- $\mathbb{E}_{\psi_Z}(T) = -E_Z$
- $\mathbb{E}_{\psi_Z}\left(\frac{Z}{2}V\right) = 2E_Z$
- $\mathbb{E}_{\psi_Z}\left(\frac{e^2}{|\underline{x}_1 - \underline{x}_2|}\right) = \frac{5}{8}\frac{Ze^2}{a} = \frac{-5E_Z}{8Z}$ (by same calc. from 1st order perturbation theory).

So altogether, $F(Z) = \frac{-e^2}{a}\left(-Z^2 + 4Z - \frac{5}{8}Z\right)$, $F'(Z) = \frac{-e^2}{a}\left(-2Z + \frac{27}{8}\right) = 0$, and we minimize by setting $Z_* = \frac{27}{16}$. Effectively, we are saying $\frac{5}{16}$ of a unit of charge is screened.

Plugging back in, $\mathcal{F}_{II}(\psi_{Z_*}) = \frac{-e^2}{a}\left(\frac{27}{16}\right)^2 \approx 2.85\left(\frac{-e^2}{a}\right)$. How does this measure up?

0th order perturbation theory:	$4.00\left(\frac{-e^2}{a}\right)$
1st order perturbation theory:	$2.75\left(\frac{-e^2}{a}\right)$ (6% error, and an overestimate, 2nd order correction < 0).
Experimental value:	$2.92\left(\frac{-e^2}{a}\right)$

Our variational result has a relative error of about 2.5%. Pretty good! Can improve more by introducing more complicated ansatz. A very powerful method when applied with enough skill!

Can also use variational methods (to an extent) to study/estimate/bound excited states. First a common trick:

▷ Suppose there is a subspace $S \subseteq \mathcal{H}$ such that $H: S \to S$. Then by taking variational ansatz that lies in S, we can bound/estimate the lowest eigenvalue of H acting on S.

Example: For harmonic oscillator with $H = \frac{1}{2}p^2 + \frac{1}{2}m\omega^2 x^2$, we define $L^2(\mathbb{R})_{even} = \{\text{wave functions even under } x \leftrightarrow -x\}$ and $L^2(\mathbb{R})_{odd} = \{\text{wave functions odd under } x \leftrightarrow -x\}$ then

$$H: L^2(\mathbb{R})_{even/odd} \to L^2(\mathbb{R})_{even/odd}$$

On homework you look at a variational estimate for the ground state:

$$\psi_\alpha^{[0]}(x) = \exp(-\alpha x^2)$$

But we can also estimate the first excited state (which is the lowest energy state in $L^2(\mathbb{R})_{odd}$). We take a simple (odd) ansatz:

$$\psi_\alpha^{[1]}(x) = x \exp(-\alpha x^2)$$

Computing Rayleigh quotient gives

$$\mathcal{J}_H(\psi_\alpha^{[1]}) = \frac{3m\omega^2}{8\alpha} + \frac{3\alpha\hbar^2}{2m} = F(\alpha), \quad F'(\alpha_*) = 0 \text{ for } \alpha_* = \frac{m\omega}{2\hbar}$$

This yields our bound/estimate:

$$E_1 \leq F(\alpha_*) = \frac{6\hbar\omega}{8} + \frac{3\hbar\omega}{4} = \frac{3}{2}\hbar\omega = E_1 \text{ exactly}$$

This is a useful trick if, for example, you are working in a system with rotational symmetry and you want to estimate the lowest energy state with a given angular momentum.

A more systematic and general approach to studying excited states with variational methods utilizes the so-called "min-max theorem" of Fischer-Courant.

[N.B.: there is a more nuanced version of the theorem when studying an operator with continuum eigenvectors. We will just give the version for discrete spectrum / finite dim'l Hilbert spaces.]

Thm. (Min-max): For self-adjoint A with discrete eigenvalues $a_1 \leq a_2 \leq a_3 \leq \dots$, we have the equality

$$a_K = \min_{S \subseteq \mathcal{H}} \left\{ \max\{ \mathcal{F}_A(\psi) \mid \psi \in S \} \;\middle|\; \dim(S) = K \right\}$$

We won't cover the proof, but note that when $S = \text{span}\{\psi_1, \psi_2, \dots, \psi_K\}$ with $A\psi_k = a_k \psi_k$, we have $\max_S \mathcal{F}_A = a_K$, so only need to show that for other choices of S, $a_K \leq \max_S \mathcal{F}_A$.

For our purposes, the point is that for any given K-dim'l subspace $S \subseteq \mathcal{H}$, we get an upper bound $a_K \leq \max_S \mathcal{F}_A$. Can compute this because $\max_S \mathcal{F}_A$ is a stationary point of $\mathcal{F}_A$ restricted to S, so it is the largest eigenvalue of the restriction of A to S.

Proof: let $\{\phi_1, \dots, \phi_K\}$ be a basis for S. Then we have that for $\psi = \sum_{r=1}^{K} c_r \phi_r$ a stationary point of $\mathcal{F}_A$ restricted to S, $(A - \mathcal{F}_A(\psi))|\psi\rangle \in S^\perp$, so

$$\langle \phi_s | A - \mathcal{F}_A(\psi) | \psi \rangle = \sum_r \langle \phi_s | A - \mathcal{F}_A(\psi) | \phi_r \rangle c_r = 0 \quad \text{for } s = 1, \dots, K$$

So $(c_1, \dots, c_K)^T$ is an eigenvector of the matrix $\langle \phi_s | A | \phi_r \rangle$ w/eigenvalue $\mathcal{F}_A(\psi)$, so maximum is given by largest eigenvalue.

Corollary: If we solve the "secular equation"

$$\det\left(\langle \phi_s | A | \phi_r \rangle - \tilde{a} \langle \phi_s | \phi_r \rangle \right) = 0 \quad \text{for } \tilde{a}$$

Then the K solutions $\tilde{a}_1 \leq \tilde{a}_2 \leq \dots \leq \tilde{a}_K$ provide upper bounds/estimates for the first K eigenvalues of A:

$$a_i \leq \tilde{a}_i \qquad i = 1, \dots, K$$

The bound for a_0 coming from this computation is just the variational bound arising from the trial state

$$\psi_{\text{ansatz}} = \sum_{r=1}^{K} \lambda_r \phi_r$$