PHY 741 Quantum Mechanics
12-12:50 AM MWF Olin 103

Plan for Lecture 25:

Chap. 17 in Shankar:
Time-Independent Perturbation Theory

1. **Case of non-degenerate spectrum**
2. **Treatment of degenerate spectrum**

17	Mon, 10/09/2017	Chap. 13	Quantum mechanics of a hydrogen atom	#10	10/16/2017
18	Wed, 10/11/2017	Chap. 13	Quantum mechanics of multi-electron atoms		
	Fri, 10/13/2017		*Fall break -- No class*		
19	Mon, 10/16/2017		Discuss exam questions and topics for presentations	Topic	10/18/2017
20	Wed, 10/18/2017	Chap. 14	Intrinsic spin	#11	10/20/2017
21	Fri, 10/20/2017	Chap. 15	Addition of Angular Momentum	#12	10/23/2017
22	Mon, 10/23/2017	Chap. 15	Multi-electron atoms	#13	10/25/2017
23	Wed, 10/25/2017	Chap. 15	Multi-electron atoms	#14	10/30/2017
24	Fri, 10/27/2017		Effects of nuclear motion		
25	Mon, 10/30/2017	Chap. 17	Time-independent perturbation theory	#15	11/3/2017
26	Wed, 11/01/2017				
27	Fri, 11/03/2017				
28	Mon, 11/06/2017				
29	Wed, 11/08/2017				
30	Fri, 11/10/2017				
31	Mon, 11/13/2017				
32	Wed, 11/15/2017				
33	Fri, 11/17/2017				
34	Mon, 11/20/2017				
	Wed, 11/22/2017		*Thanksgiving Holiday -- No class*		

Methods for finding approximate solutions to the time-independent Schrödinger equation

Bound states	Continuum states
Variational methods	Scattering theory
Perturbation theory	

$$H\left|n\right\rangle = E_n\left|n\right\rangle$$

$$H = H^0 + \epsilon H^1$$

In general, we approach the problem using the complete basis set of H^0:

$$H^0\left|n^0\right\rangle = E_n^0\left|n^0\right\rangle$$

$$H\left|n\right\rangle = E_n\left|n\right\rangle$$
$$H = H^0 + \epsilon H^1$$

Assume: $\left|n\right\rangle = \left|n^0\right\rangle + \epsilon\left|n^1\right\rangle + \epsilon^2\left|n^2\right\rangle + \ldots$

$$E_n = E_n^0 + \epsilon E_n^1 + \epsilon^2 E_n^2 + \ldots$$

Note: This methods depends on the non-degenerate case: $E_n \neq E_m$ for $n \neq m$

First order corrections

$$\left(H^0 + \epsilon H^1\right)\left(\left|n^0\right\rangle + \epsilon\left|n^1\right\rangle + \epsilon^2\left|n^2\right\rangle + \ldots\right)$$
$$= \left(E_n^0 + \epsilon E_n^1 + \epsilon^2 E_n^2 + \ldots\right)\left(\left|n^0\right\rangle + \epsilon\left|n^1\right\rangle + \epsilon^2\left|n^2\right\rangle + \ldots\right)$$

Collecting terms according to their order:

$$\epsilon^0: \quad H^0\left|n^0\right\rangle = E_n^0\left|n^0\right\rangle$$
$$\epsilon^1: \quad H^0\left|n^1\right\rangle + H^1\left|n^0\right\rangle = E_n^0\left|n^1\right\rangle + E_n^1\left|n^0\right\rangle$$
$$\left\langle n^0\right|H^0\left|n^1\right\rangle + \left\langle n^0\right|H^1\left|n^0\right\rangle = \left\langle n^0\right|E_n^0\left|n^1\right\rangle + \left\langle n^0\right|E_n^1\left|n^0\right\rangle$$
$$\Rightarrow E_n^1 = \left\langle n^0\right|H^1\left|n^0\right\rangle$$

First order corrections -- continued

Since the eigenstates $\left|n^0\right\rangle$ for a complete set of states:

Assume $\left|n^1\right\rangle = \sum_{m \neq n} C_m \left|m^0\right\rangle$

$$C_m = \frac{\left\langle m^0\right|H_1\left|n^0\right\rangle}{E_n^0 - E_m^0}$$

$$\left|n^1\right\rangle = \sum_{m \neq n}\left(\frac{\left\langle m^0\right|H_1\left|n^0\right\rangle}{E_n^0 - E_m^0}\right)\left|m^0\right\rangle$$

Second order corrections

$$\epsilon^2: \quad H^0\left|n^2\right\rangle + H^1\left|n^1\right\rangle = E_n^0\left|n^2\right\rangle + E_n^1\left|n^1\right\rangle + E_n^2\left|n^0\right\rangle$$

$$\left\langle n^0\right|H^0\left|n^2\right\rangle + \left\langle n^0\right|H^1\left|n^1\right\rangle = \left\langle n^0\right|E_n^0\left|n^2\right\rangle + \left\langle n^0\right|E_n^1\left|n^1\right\rangle + \left\langle n^0\right|E_n^2\left|n^0\right\rangle$$

$$\Rightarrow E_n^2 = \left\langle n^0\right|H^1\left|n^1\right\rangle = \sum_{m\neq n} \frac{\left\langle n^0\right|H^1\left|m^0\right\rangle\left\langle m^0\right|H^1\left|n^0\right\rangle}{E_n^0 - E_m^0}$$

$$\left|n^2\right\rangle = \sum_{m\neq n}\left|m^0\right\rangle \sum_{l\neq n} \frac{\left\langle m^0\right|H^1\left|l^0\right\rangle\left\langle l^0\right|H^1\left|n^0\right\rangle}{\left(E_n^0 - E_m^0\right)\left(E_n^0 - E_l^0\right)}$$

$$-\sum_{m\neq n}\left|m^0\right\rangle \frac{\left\langle m^0\right|H^1\left|n^0\right\rangle\left\langle n^0\right|H^1\left|n^0\right\rangle}{\left(E_n^0 - E_m^0\right)^2} - \frac{1}{2}\left|n^0\right\rangle \sum_{m\neq n} \frac{\left|\left\langle m^0\right|H^1\left|n^0\right\rangle\right|^2}{\left(E_n^0 - E_m^0\right)^2}$$

Due to normalization

Example – Harmonic oscillator

$$H^0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

$$H^1 = \frac{1}{2}m\Omega^2 x^2$$

Exact eigenstates: $E_n^{\text{exact}} = \hbar\sqrt{\omega^2 + \Omega^2}\left(n + \frac{1}{2}\right)$

$$= \hbar\omega\left(1 + \frac{1}{2}\frac{\Omega^2}{\omega^2} - \frac{1}{8}\frac{\Omega^4}{\omega^4}\ldots\right)\left(n + \frac{1}{2}\right)$$

Perturbation theory results:

$$E_n^1 = \left\langle n^0\right|\tfrac{1}{2}m\Omega^2 x^2\left|n^0\right\rangle = \hbar\omega\frac{\Omega^2}{2\omega^2}\left(n + \frac{1}{2}\right)$$

Example: He atom

$$H(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$H^0(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2}$$

$$H^1(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

What happens when the spectrum of H^0 has degeneracy?

$$\left(H^0 + \epsilon H^1\right)\left(\left|n^0\right\rangle + \epsilon\left|n^1\right\rangle + \epsilon^2\left|n^2\right\rangle + \ldots\right)$$
$$= \left(E_n^0 + \epsilon E_n^1 + \epsilon^2 E_n^2 + \ldots\right)\left(\left|n^0\right\rangle + \epsilon\left|n^1\right\rangle + \epsilon^2\left|n^2\right\rangle + \ldots\right)$$

Collecting terms according to their order:

$$\epsilon^0: \quad H^0\left|n^0\right\rangle = E_n^0\left|n^0\right\rangle$$
$$\epsilon^1: \quad H^0\left|n^1\right\rangle + H^1\left|n^0\right\rangle = E_n^0\left|n^1\right\rangle + E_n^1\left|n^0\right\rangle$$

Since the eigenstates $\left|n^0\right\rangle$ for a complete set of states:

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$$C_m = \frac{\left\langle m^0\right|H_1\left|n^0\right\rangle}{E_n^0 - E_m^0}$$

$$\left|n^1\right\rangle = \sum_{m \neq n}\left(\frac{\left\langle m^0\right|H_1\left|n^0\right\rangle}{E_n^0 - E_m^0}\right)\left|m^0\right\rangle$$

→ problem when $E^0_n = E^0_m$
→ solution – consider the degenerate states separately