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

Plan for Lecture 26:

Chap. 17 in Shankar:
Time-Independent Perturbation Theory

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

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Events

Meet the Speaker: Nov 1 at Noon
WFU Physics Meet the Speaker Event SPEAKER: Dr. Yves Chabal Department of Materials Science and Engineering, University of Texas at Dallas, Dallas, TX TIME: Wed. Nov. 1, 2017, 12:00 – 1:00 ...

Colloquium: Nov. 1, 2017 at 4 PM
WFU Physics Colloquium TITLE: "The fascinating world of Metal Organic Framework materials" SPEAKER: Yves Chabal Department of Materials Science and Engineering, University of Texas at Dallas, Dallas, TX TIME: Wed. ...

	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	Chap. 17	Time-independent perturbation theory		
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*		
	Fri, 11/24/2017		*Thanksgiving Holiday -- No class*		
35	Mon, 11/27/2017				

Approximation schemes for solving the time-independent Schrödinger equation

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

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

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

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

However, consider the case when

$E^0_{n_a} = E^0_{n_b} ....E^0_{n_N}$

Degenerate perturbation theory,

considering the effects on the N-fold degenerate states:

$\left|n_a^0\right\rangle, \left|n_b^0\right\rangle, ...\left|n_N^0\right\rangle$ where $E^0_{n_a} = E^0_{n_b} ... = E^0_{n_N}$

For $i = 1, 2, ...N$, assume $\left|n_i^1\right\rangle = \sum_{j=1}^{N} C_j^i \left|n_j^0\right\rangle$

$\Rightarrow$ The N first-order wavefunctions will be the eigenstates of the $N \times N$ matrix $\left\langle n_j^0\right| H^0 + H^1 \left|n_i^0\right\rangle$

Example of degenerate perturbation theory in the treatment of the term values of multi-electron atoms:

$$\boldsymbol{\mathcal{H}} = \underbrace{\sum_i h(\mathbf{r}_i)}_{\text{single electron terms}} + \sum_{i,j<i} \frac{e^2}{\underbrace{\left|\mathbf{r}_i - \mathbf{r}_j\right|}_{\text{electron-electron interaction}}} \qquad h(\mathbf{r}_i) \equiv -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i}$$

Evaluating expectation values: $\left\langle LM\right|\boldsymbol{\mathcal{H}}\left|LM\right\rangle$ for $2p^2$

$$E(P) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) - \frac{5}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

$$E(D) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{1}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

$$E(S) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{10}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

Example of degenerate perturbation theory in the treatment of the effects of spin-orbit interaction:

$$H_{SO} = G(r)\mathbf{S}\cdot\mathbf{L}$$

Note that: $\mathbf{J} = \mathbf{S} + \mathbf{L}$

$$\mathbf{J}^2 = \mathbf{S}^2 + \mathbf{L}^2 + 2\mathbf{S}\cdot\mathbf{L}$$

$$\langle JM;ls | H_{SO} | JM;ls\rangle = G(r)\langle JM;ls|\mathbf{S}\cdot\mathbf{L}|JM;ls\rangle$$

$$= \frac{\hbar^2 G(r)}{2}\left(j(j+1) - s(s+1) - l(l+1)\right)$$

J=l+1/2:

$$\left\langle \left(l+\tfrac{1}{2}\right)M;ls \middle| H_{SO} \middle| \left(l+\tfrac{1}{2}\right)M;ls\right\rangle = \frac{\hbar^2 G(r)}{2} l$$

J=l-1/2:

$$\left\langle \left(l-\tfrac{1}{2}\right)M;ls \middle| H_{SO} \middle| \left(l-\tfrac{1}{2}\right)M;ls\right\rangle = -\frac{\hbar^2 G(r)}{2}(l+1)$$

Example of degenerate perturbation theory for a H atom in the degenerate states

$$|nlm\rangle = |200\rangle, |21-1\rangle, |210\rangle, |211\rangle$$

all having zero-order energies $E_2^0 = -\frac{e^2}{2a_0}\frac{1}{2^2}$

In this case, consider a perturbation caused by an electrostatic field F directed along the z-axis causing polarization of the electron:

$$H^1 = eFr\cos\theta$$

Matrix elements:

$$\langle 2lm|H^1|2l'm'\rangle = -3eFa_0\delta_{|l-l'|1}\delta_{m0}\delta_{m'0}$$

Details:

$$\langle 200|H^1|210\rangle = \frac{eF}{16a_0^4}\int_0^\infty r^4 dr\left(2-\frac{r}{a_0}\right)e^{-r/a_0}\int_{-1}^{1}\cos^2\theta\, d\cos\theta$$

$$= -3eFa_0$$

Degenerate perturbation theory example for the Stark effect -- continued

Matrix elements:

$$\langle 2lm|H^1|2l'm'\rangle = \begin{array}{c|cccc} & |200\rangle & |210\rangle & |21-1\rangle & |211\rangle \\ \hline \langle 200| & 0 & -3eFa_0 & 0 & 0 \\ \langle 210| & -3eFa_0 & 0 & 0 & 0 \\ \langle 21-1| & 0 & 0 & 0 & 0 \\ \langle 211| & 0 & 0 & 0 & 0 \end{array}$$

Eigenvalues of $\langle 2lm|H^0 + H^1|2l'm'\rangle$:

E_2^0 for $|21\pm1\rangle$

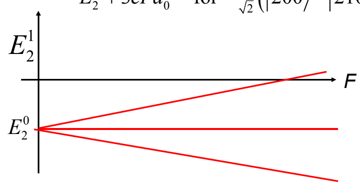
$E_2^0 - 3eFa_0$ for $\frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right)$

$E_2^0 + 3eFa_0$ for $\frac{1}{\sqrt{2}}\left(|200\rangle - |210\rangle\right)$

Degenerate perturbation theory example for the Stark effect -- continued

Eigenvalues of $\langle 2lm | H^0 + H^1 | 2l'm' \rangle$:

$$E_2^1 = \begin{cases} E_2^0 & \text{for} \quad |21\pm1\rangle \\ E_2^0 - 3eFa_0 & \text{for} \quad \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right) \\ E_2^0 + 3eFa_0 & \text{for} \quad \frac{1}{\sqrt{2}}\left(|200\rangle - |210\rangle\right) \end{cases}$$



Degenerate perturbation theory example for effects of a constant magnetic field B on an atom

$$H = \frac{\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2}{2m} + V(r) + \frac{e}{mc}\mathbf{B}\cdot\mathbf{S} \qquad \text{Vector potential } \mathbf{A} = \frac{1}{2}\mathbf{r}\times\mathbf{B}$$

$$H^0 = \frac{\mathbf{p}^2}{2m} + V(r)$$

Keeping only terms to linear order in $\mathbf{B}$:

$$H^1 = \frac{e}{2mc}\left(\mathbf{L} + 2\mathbf{S}\right)\cdot\mathbf{B}$$

Detail:

$$\frac{1}{2}\mathbf{p}\cdot\mathbf{r}\times\mathbf{B} + \frac{1}{2}\mathbf{r}\times\mathbf{B}\cdot\mathbf{p} = \mathbf{L}\cdot\mathbf{B}$$

Degenerate perturbation theory example for effects of a constant magnetic field B on an atom -- continued

For atoms with total orbital momentum L and total spin S:

$$\mathbf{L}^2 |LM;SM_S\rangle = \hbar^2 L(L+1)|LM;SM_S\rangle \qquad L_z|LM;SM_S\rangle = \hbar M|LM;SM_S\rangle$$

$$\mathbf{S}^2 |LM;SM_S\rangle = \hbar^2 S(S+1)|LM;SM_S\rangle \qquad S_z|LM;SM_S\rangle = \hbar M_S|LM;SM_S\rangle$$

These states have a degeneracy of $(2L+1)(2S+1)$

Degenerate perturbation theory matrix for first order:

$$\langle LM;SM_S|H^1|LM';SM_S'\rangle = \frac{e\hbar B}{2mc}(M + 2M_S)\delta_{MM'}\delta_{M_SM_S'}$$

Example: atomic term: ${}^3P$

values of $\langle LM;SM_S|H^1|LM';SM_S'\rangle / (e\hbar B/2mc)$

$M_S =$	-1	0	1
$M=-1$	-3	-1	1
$M=0$	-2	0	2
$M=1$	-1	1	3

Paschen-Back effect

Degenerate perturbation theory example for effects of a constant magnetic field B on an atom – including the effects of spin-orbit interaction

$$H = \frac{\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2}{2m} + V(r) + G(r)\mathbf{S}\cdot\mathbf{L} + \frac{e}{mc}\mathbf{B}\cdot\mathbf{S}$$

$$H^0 = \frac{\mathbf{p}^2}{2m} + V(r)$$

Keeping only terms to linear order in $\mathbf{B}$:

$$H^1 = G(r)\mathbf{S}\cdot\mathbf{L} + \frac{e}{2mc}\left(\mathbf{L} + 2\mathbf{S}\right)\cdot\mathbf{B}$$

$$= \frac{G(r)}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right) + \frac{e}{2mc}\left(\mathbf{J} + \mathbf{S}\right)\cdot\mathbf{B}$$