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

Plan for Lecture 36:

General Review

Schedule for PHY 741 presentations
Monday Dec. 4, 2017

Time	Presenter	Title
12:00-12:15 PM	TJ Colvin	
12:17-12:32 PM	Sajant Anand anans14@	Numerical Simulations of a Quantum Particle in a Box
12:34-12:49 PM		

Wednesday Dec. 6, 2017

Time	Presenter	Title
12:00-12:15 PM	Haardik Pandey	DFT calculations for Water molecule
12:1712:32 PM	Yan Li	Numerical solutions for a finite square well problem
12:34-12:49 PM	Ellie Alipour	

Friday Dec. 8, 2017

Time	Presenter	Title
12:00-12:15 PM	Kevin Roebuck	Spin splitting of open shell atoms in a magnetic field
12:17-12:32 PM	Matthew Waldrip	IR spectra of ____
12:34-12:49 PM	Nouf Alharbi	

Please refer to Lecture 15 for review of material from first portion of the course

Approximation methods for finding eigenstates of the Hamiltonian (or stationary states of the Schödinger equation)

1. Variational methods
2. Perturbation expansions

Variational methods are based on the following:
For any function $|\Psi_{trial}\rangle$ it can be shown
that the lowest eigenvalue E_0 can be estimate from:

$$\frac{\langle\Psi_{trial}|H|\Psi_{trial}\rangle}{\langle\Psi_{trial}|\Psi_{trial}\rangle} \leq E_0$$

Non-degenerate 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:

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

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

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

Non-degenerate perturbation theory continued:

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

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

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

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

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

Due to normalization

Degenerate perturbation theory,
considering the effects on the N-fold degenerate states:
$\left|n_a^0\right\rangle, \left|n_b^0\right\rangle, \ldots \left|n_N^0\right\rangle$ where $E_{n_a}^0 = E_{n_b}^0 \ldots = E_{n_N}^0$

For $i = 1, 2, \ldots N$, 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 $\left\langle n_j^0\right|H^0 + H^1\left|n_i^0\right\rangle$

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

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

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

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

$$H^1 = G(r)\mathbf{S}\cdot\mathbf{L} + \mu_B\left(\mathbf{L} + g\mathbf{S}\right)\cdot\mathbf{B}/\hbar$$

$$= \frac{G(r)}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right) + \mu_B\left(\mathbf{J} + (g-1)\mathbf{S}\right)\cdot\mathbf{B}/\hbar$$

Perturbation theory treatment of uniform and constant magnetic fields on atomic states -- continued

$$H = H^0 + H^1$$

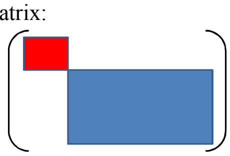
$$H^0 = \frac{\mathbf{p}^2}{2m} + V(r)$$

$$H^1 = G(r)\mathbf{S}\cdot\mathbf{L} + \mu_B\left(\mathbf{L} + g\mathbf{S}\right)\cdot\mathbf{B}/\hbar$$

For the effects on a H atom in the $n=2$ states:

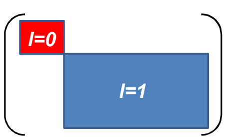
$\Rightarrow 8\times 8$ perturbation matrix:

$$\langle 2lmm_s | H^1 | 2lm'm_s' \rangle =$$



$$H^1 = G(r)\mathbf{S}\cdot\mathbf{L} + \mu_B\left(\mathbf{L} + g\mathbf{S}\right)\cdot\mathbf{B}/\hbar$$

$$\langle 2lmm_s | H^1 | 2lm'm_s' \rangle =$$



$$\langle 200m_s | H^1 | 200m_s' \rangle = \begin{array}{c c} & m_s' = \tfrac{1}{2} \quad -\tfrac{1}{2} \\ \begin{array}{c} m_s = \tfrac{1}{2} \\ m_s = -\tfrac{1}{2} \end{array} & \begin{pmatrix} \frac{g\mu_B B}{2} & 0 \\ 0 & -\frac{g\mu_B B}{2} \end{pmatrix} \end{array}$$

$$H^1 = G(r)\mathbf{S}\cdot\mathbf{L} + \mu_B\left(\mathbf{L}+g\mathbf{S}\right)\cdot\mathbf{B}/\hbar$$

$$\langle 21mm_s|H^1|21m'm_s'\rangle = \begin{array}{c|c} & m'm_s' = 1\tfrac{1}{2}\quad 1-\tfrac{1}{2}\quad 0\tfrac{1}{2}\quad 0-\tfrac{1}{2}\quad -1\tfrac{1}{2}\quad -1-\tfrac{1}{2} \\ \begin{array}{r} mm_s = 1\tfrac{1}{2} \\ 1-\tfrac{1}{2} \\ 0\tfrac{1}{2} \\ 0-\tfrac{1}{2} \\ -1\tfrac{1}{2} \\ -1-\tfrac{1}{2} \end{array} & \begin{pmatrix} X & & & & & \\ & X & X & & & \\ & X & X & & & \\ & & & X & X & \\ & & & X & X & \\ & & & & & X \end{pmatrix} \end{array}$$

$$\mathbf{S}\cdot\mathbf{L} = \tfrac{1}{2}\left(S_-L_+ + S_+L_-\right) + S_zL_z$$

$$J_\pm|jm\rangle = \hbar\sqrt{j^2 - m^2 + j \mp m}\,|j(m\pm 1)\rangle$$

$$H^1 = G(r)\mathbf{S}\cdot\mathbf{L} + \mu_B\left(\mathbf{L}+g\mathbf{S}\right)\cdot\mathbf{B}/\hbar$$

Let $\gamma \equiv \dfrac{\langle 21|G(r)|21\rangle}{2\hbar^2}$

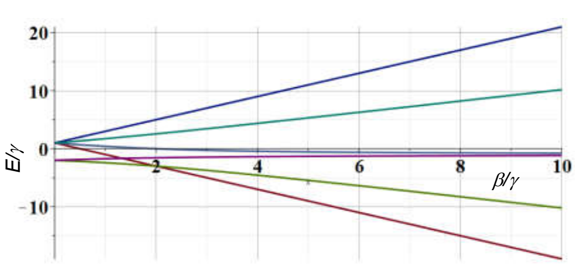
$\beta \equiv \mu_B \mathrm{B}_0$

$$\langle 21mm_s|H^1|21m'm_s'\rangle =$$

$$\begin{array}{c|c} & m'm_s' = 1\tfrac{1}{2}\quad 1-\tfrac{1}{2}\quad 0\tfrac{1}{2}\quad 0-\tfrac{1}{2}\quad -1\tfrac{1}{2}\quad -1-\tfrac{1}{2} \\ \begin{array}{r} mm_s = 1\tfrac{1}{2} \\ 1-\tfrac{1}{2} \\ 0\tfrac{1}{2} \\ 0-\tfrac{1}{2} \\ -1\tfrac{1}{2} \\ -1-\tfrac{1}{2} \end{array} & \begin{pmatrix} \gamma+\beta(1+g/2) & 0 & 0 & 0 & 0 & 0 \\ 0 & -\gamma+\beta(1-g/2) & \sqrt{2}\gamma & 0 & 0 & 0 \\ 0 & \sqrt{2}\gamma & \beta g/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\beta g/2 & \sqrt{2}\gamma & 0 \\ 0 & 0 & 0 & \sqrt{2}\gamma & -\gamma-\beta(1-g/2) & 0 \\ 0 & 0 & 0 & 0 & 0 & \gamma-\beta(1+g/2) \end{pmatrix} \end{array}$$

$$H^1 = G(r)\mathbf{S}\cdot\mathbf{L} + \mu_B\left(\mathbf{L}+g\mathbf{S}\right)\cdot\mathbf{B}/\hbar$$

Evaluated for degenerate states $|nlmm_s\rangle = |21mm_s\rangle$



Often the degenerate states are related by symmetry, and we can use the properties of appropriate operators to prepare the eigenstates. For example, the notion of "addition" of angular momentum is related to this idea.

In the absence of external magnetic fields, the internal magnetic dipoles cause spin interactions within each system, however, the total angular momentum of the system should be conserved.

Clebsch-Gordan coefficients

$$|JM, j_1 j_2\rangle = \sum_{m_1, m_2} |j_1 m_1, j_2 m_2\rangle \langle j_1 m_1, j_2 m_2 | JM, j_1 j_2\rangle$$

Finding the total angular momentum – "addition" of angular momentum. $\mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2$

$$\mathbf{J}^2 |JM\rangle = \hbar^2 J(J+1) |JM\rangle$$

$$J_z |JM\rangle = \hbar M |JM\rangle$$

$$\mathbf{j}_1{}^2 |j_1 m_1\rangle = \hbar^2 j_1(j_1+1) |j_1 m_1\rangle$$

$$j_{1z} |j_1 m_1\rangle = \hbar m_1 |j_1 m_1\rangle$$

Finding the Clebsch-Gordan coefficients in general follows the equations:

Reference: Abramowitz & Stegum – pg. 1006

Original formula:

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle = \delta_{m, m_1+m_2} \sqrt{\frac{(j_1+j_2-j)!(j_1-j_2+j)!(-j_1+j_2+j)!(2j+1)}{(j_1+j_2+j+1)!}}$$
$$\times \sum_k \frac{(-1)^k \sqrt{(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j+m)!(j-m)!}}{k!(j_1+j_2-j-k)!(j_1-m_1-k)!(j_2+m_2-k)!(j-j_2+m_1+k)!(j-j_1-m_2+k)!}$$

Working formula:

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle = \delta_{m, m_1+m_2} \sqrt{\frac{(j_1-j_2+j)!(-j_1+j_2+j)!(2j+1)}{(j_1+j_2-j)!(j_1+j_2+j+1)!}}$$
$$\times \sqrt{\frac{(j_1+m1)!(j_2-m_2)!(j+m)!}{(j_1-m1)!(j_2+m_2)!(j-m)!}}$$
$$\times \sum_k \frac{(-1)^k}{k!} \frac{(j_1+j_2-j)!}{(j_1+j_2-j-k)!} \frac{(j_1-m_1)!}{(j_1-m_1-k)!} \frac{(j_2+m_2)!}{(j_2+m_2-k)!} \frac{(j-m)!}{(j-j_2+m_1+k)!(j-j_1-m_2+k)!}$$

Details for a simple case:

Clebsch-Gordan coefficients

$$|JM, j_1 j_2\rangle = \sum_{m_1, m_2} |j_1 m_1, j_2 m_2\rangle\langle j_1 m_1, j_2 m_2|JM, j_1 j_2\rangle \quad M = m_1 + m_2$$

Recall that:

$$J_\pm |JM\rangle = \hbar\sqrt{J^2 - M^2 + J \mp M}\,|J(M \pm 1)\rangle$$

$$J_\pm = j_{1\pm} + j_{2\pm}$$

$$|11;\tfrac{1}{2}\tfrac{1}{2}\rangle = |\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\rangle$$

$$J_- |11;\tfrac{1}{2}\tfrac{1}{2}\rangle = \hbar\sqrt{2}\,|10;\tfrac{1}{2}\tfrac{1}{2}\rangle$$

$$(j_{1-} + j_{2-})|\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\rangle = \hbar|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\rangle + \hbar|\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

$$\Rightarrow |10;\tfrac{1}{2}\tfrac{1}{2}\rangle = \frac{1}{\sqrt{2}}\left(|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\rangle + |\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\rangle\right)$$

$$|1-1;\tfrac{1}{2}\tfrac{1}{2}\rangle = |\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

Summary of results:

$$\left.\begin{aligned}
&|11;\tfrac{1}{2}\tfrac{1}{2}\rangle = |\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\rangle \\
&|10;\tfrac{1}{2}\tfrac{1}{2}\rangle = \frac{1}{\sqrt{2}}\left(|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\rangle + |\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\rangle\right) \\
&|1-1;\tfrac{1}{2}\tfrac{1}{2}\rangle = |\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\rangle
\end{aligned}\right\} \textit{J=1 } \text{degeneracy: } \textit{2J+1=3}$$

$$\left.|00;\tfrac{1}{2}\tfrac{1}{2}\rangle = \frac{1}{\sqrt{2}}\left(|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\rangle - |\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\rangle\right)\right\} \textit{J=0 } \text{degeneracy: } \textit{2J+1=1}$$

Note that these eigenstates have different behaviors wrt to particle exchange:

$|1M;\tfrac{1}{2}\tfrac{1}{2}\rangle \Rightarrow$ even under particle exchange

$|00;\tfrac{1}{2}\tfrac{1}{2}\rangle \Rightarrow$ odd under particle exchange

Case of "addition" of spin and orbital angular momentum

$j_1 = l \qquad j_2 = s = \tfrac{1}{2}$

$$|(l+\tfrac{1}{2})M;l\tfrac{1}{2}\rangle = \sqrt{\frac{l+M+\frac{1}{2}}{2l+1}}\,|l(M-\tfrac{1}{2});\tfrac{1}{2}\tfrac{1}{2}\rangle + \sqrt{\frac{l-M+\frac{1}{2}}{2l+1}}\,|l(M+\tfrac{1}{2});\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

$$|(l-\tfrac{1}{2})M;l\tfrac{1}{2}\rangle = -\sqrt{\frac{l-M+\frac{1}{2}}{2l+1}}\,|l(M-\tfrac{1}{2});\tfrac{1}{2}\tfrac{1}{2}\rangle + \sqrt{\frac{l+M+\frac{1}{2}}{2l+1}}\,|l(M+\tfrac{1}{2});\tfrac{1}{2}-\tfrac{1}{2}\rangle$$

Spin-orbit interaction due to spin alignment in magnetic field generated by orbital motion

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

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

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

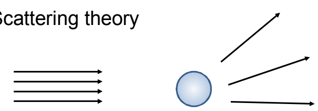
$$\langle JM;ls|H_{SO}|JM;ls\rangle = G(r)\langle JM;ls|\mathbf{S}\cdot\mathbf{L}|JM;ls\rangle$$

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

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

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

Scattering theory



$e^{i\mathbf{k}\cdot\mathbf{r}}$ $\qquad f(\hat{\mathbf{k}})\dfrac{e^{ikr}}{r}$

$$f(\hat{\mathbf{k}}) = \frac{4\pi}{k}\sum_{lm} e^{i\delta_l(E)}\sin(\delta_l(E))Y^*_{lm}(\hat{\mathbf{k}})Y_{lm}(\hat{\mathbf{r}})$$

Differential scattering cross section

$$\frac{d\sigma}{d\Omega} = \frac{\text{Probability of particle scattering}}{\text{Incident flux of particles}} = \left|f(\hat{\mathbf{k}},\hat{\mathbf{r}})\right|^2$$

$$= \left(\frac{4\pi}{k}\right)^2\left|\sum_{lm} e^{i\delta_l(E)}\sin(\delta_l(E))Y^*_{lm}(\hat{\mathbf{k}})Y_{lm}(\hat{\mathbf{r}})\right|^2$$

Determination of phase shifts:

Determination of the phase shifts:

$$\tan\delta_l(E) = \frac{L_l(E)j_l(kD) - kj_l'(kD)}{L_l(E)y_l(kD) - ky_l'(kD)}$$

where $\dfrac{d\ln\left(R_{El}(r)\right)}{dr} = \left.\dfrac{\dfrac{dR_{El}(r)}{dr}}{R_{El}(r)}\right|_{r=D} \equiv L_l(E)$

Consideration of effects of a static magnetic field on quantum states of a charged free particle. First consider the spatial degrees of freedom (ignoring intrinsic spin).

Assume particle has charge q and mass m:

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}(\mathbf{r})\right)^2$$

For a constant and uniform magnetic field $B_0\hat{\mathbf{z}}$

can choose $\mathbf{A}(\mathbf{r}) = -B_0 y\hat{\mathbf{x}}$

$$H = \frac{1}{2m}\left(p_x + \frac{qB_0 y}{c}\right)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

$$H = \frac{1}{2m}\left(p_x + \frac{qB_0 y}{c}\right)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

Constants of the motion: p_x, p_z

$$\Psi(x,y,z) = e^{i(p_x x + p_z z)/\hbar}\chi(y)$$

Energy eigenstates: $H\Psi = E\Psi$

$$E_n(p_z) = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{p_z^2}{2m}$$

where $\omega_c \equiv \dfrac{qB_0}{mc}$