PHY 742 Quantum Mechanics II
12-12:50 PM MWF Olin 103

Plan for Lecture 5
Approximate solutions for stationary states
Perturbation theory examples (Chap. 13) –

1. The Van der Waals interaction
2. The Zeeman and Paschen-Back effects
3. The hyperfine interaction

Course schedule for Spring 2022

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	Reading	Topic	HW	Due date
1	Mon: 01/10/2022	Chap. 12	Approximate solutions for stationary states -- The variational approach	#1	01/14/2022
2	Wed: 01/12/2022	Chap. 12 C	Approximate solutions for stationary states -- Perturbation theory	#2	01/19/2022
3	Fri: 01/14/2022	Chap. 12 D	Approximate solutions for stationary states -- Degenerate perturbation theory	#3	01/21/2022
	Mon: 01/17/2022		MLK Holiday -- no class		
4	Wed: 01/19/2022	Chap. 12 C & D	Approximate solutions for stationary states -- Additional tricks	#4	01/24/2022
5	Fri: 01/21/2022	Chap. 13	Examples of of the use of perturbation theory	#5	01/26/2022
6	Mon: 01/24/2022	Chap. 12 B	WKB approximation		
7	Wed: 01/26/2022	Chap. 14	Scattering theory		

PHY 742 -- Assignment #5

January 21, 2022

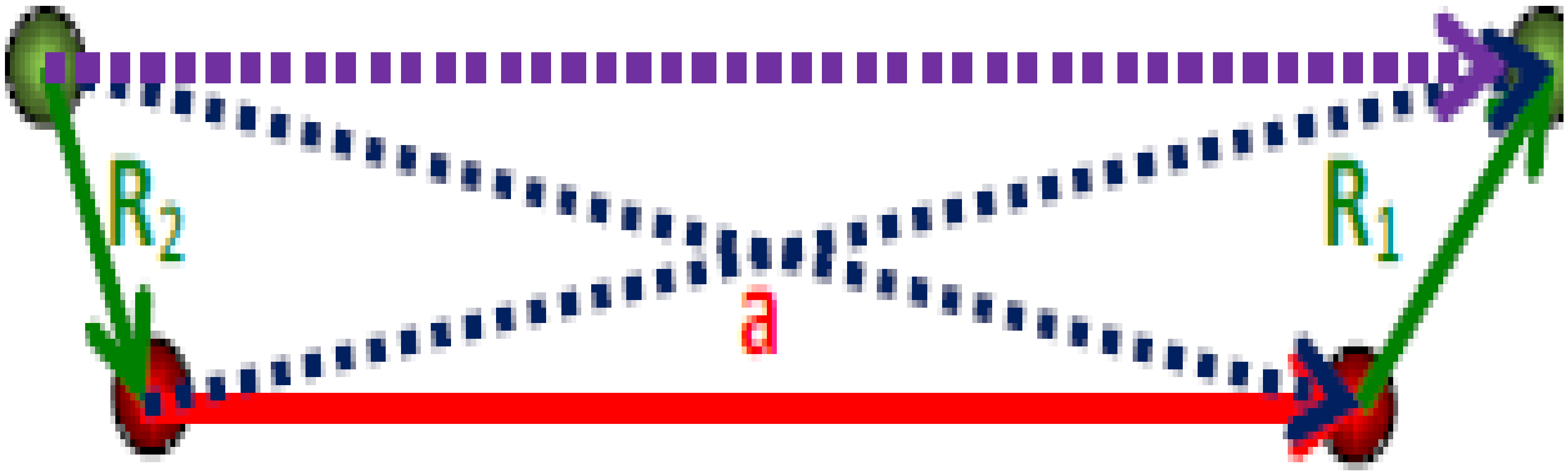
Read Chapter 13 in **Carlson's** textbook.

1. Derive some of the steps for estimating the Van der Waals interaction for two ground state H atoms separated by a distance a as discussed in your text book and in class.

The Van der Waals interaction –

➔The dominant interaction between two neutral but polarizable systems

$$W_{\mathrm{VdW}} = -\frac{A}{R^6}$$ approximately due to two induced dipoles at distance R



$$H = \frac{\mathbf{P}_1^2 + \mathbf{P}_2^2}{2m} - \frac{k_e e^2}{|\mathbf{R}_1|} - \frac{k_e e^2}{|\mathbf{R}_2|} + \left(\frac{k_e e^2}{|\mathbf{a}|} - \frac{k_e e^2}{|\mathbf{a} + \mathbf{R}_1|} - \frac{k_e e^2}{|\mathbf{a} + \mathbf{R}_2|} + \frac{k_e e^2}{|\mathbf{a} + \mathbf{R}_1 + \mathbf{R}_2|} \right)$$

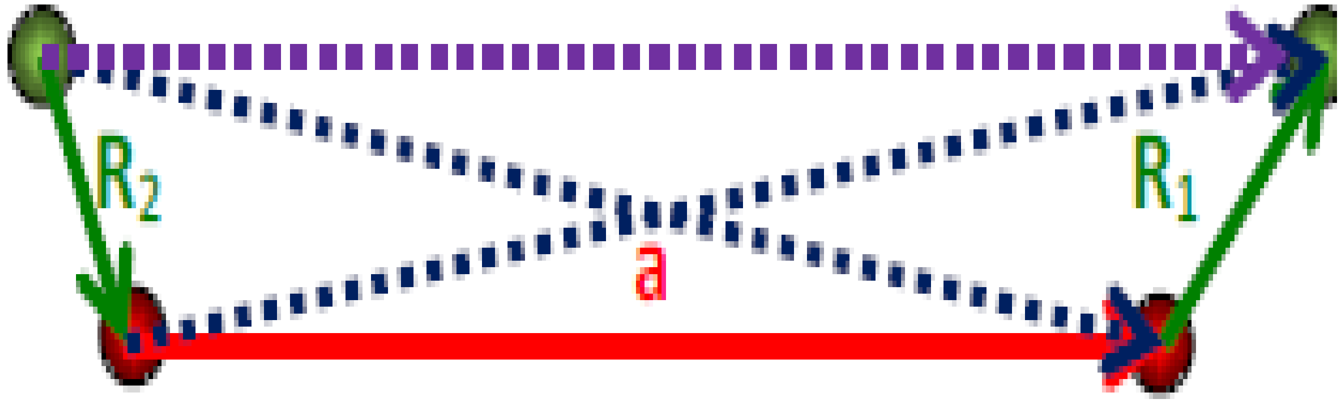


Figure 13-3: The various distances involved in the interaction of two atoms. The nuclei (red) are separated by **a**, and the electrons (green) are separated from their respective nuclei. The nuclei repel each other, (red arrow), and they attract their respective electrons (green arrows). They also attract the distant electrons (dashed blue arrow) and the electrons repel each other (dashed purple arrow).

$$H = \frac{\mathbf{P}_1^2 + \mathbf{P}_2^2}{2m} - \frac{k_e e^2}{|\mathbf{R}_1|} - \frac{k_e e^2}{|\mathbf{R}_2|} + \left(\frac{k_e e^2}{|\mathbf{a}|} - \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_1|} - \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_2|} + \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_1+\mathbf{R}_2|} \right)$$

$$H_0 = \frac{\mathbf{P}_1^2 + \mathbf{P}_2^2}{2m} - \frac{k_e e^2}{|\mathbf{R}_1|} - \frac{k_e e^2}{|\mathbf{R}_2|}$$

Zero order Hamiltonian

$$W = \frac{k_e e^2}{|\mathbf{a}|} - \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_1|} - \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_2|} + \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_1+\mathbf{R}_2|}$$

Perturbation Hamiltonian

Zero order wavefunction

$$|0\rangle = |100;100\rangle = \frac{1}{\pi a_0^3} e^{-R_1/a_0 - R_2/a_0}$$

Leading contributions to perturbing Hamiltonian

$$W = \frac{k_e e^2}{|\mathbf{a}|} - \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_1|} - \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_2|} + \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}_1+\mathbf{R}_2|}$$

$$\frac{1}{|\mathbf{a}+\mathbf{R}|} = \left[(a+Z)^2 + X^2 + Y^2\right]^{-\frac{1}{2}} = \frac{1}{a}\left[1+\frac{2Z}{a}+\frac{\mathbf{R}^2}{a^2}\right]^{-\frac{1}{2}} = \frac{1}{a}\left[1-\frac{Z}{a}-\frac{\mathbf{R}^2}{2a^2}+\frac{3Z^2}{2a^2}\right]+\cdots.$$

$$W = \frac{k_e e^e}{a}\left\{1-1+\frac{Z_1}{a}+\frac{\mathbf{R}_1^2-3Z_1^2}{2a^2}-1+\frac{Z_2}{a}+\frac{\mathbf{R}_2^2-3Z_2^2}{2a^2}+1-\frac{Z_1+Z_2}{a}-\frac{(\mathbf{R}_1+\mathbf{R}_2)^2-3(Z_1+Z_2)^2}{2a^2}\right\}$$

$$= \tfrac{1}{2}k_e e^2 a^{-3}\left(6Z_1Z_2 - 2\mathbf{R}_1\cdot\mathbf{R}_2\right) = k_e e^2 a^{-3}\left(2Z_1Z_2 - X_1X_2 - Y_1Y_2\right).$$

Estimating leading term of perturbation energy --

$$\tilde{W} = \frac{k_e e^2}{a^3}\left(2Z_1Z_2 - X_1X_2 - Y_1Y_2\right)$$

Zero-order wavefunction: $\left|0\right\rangle = \left|100;100\right\rangle = \frac{1}{\pi a_0^3} e^{-R_1/a_0 - R_2/a_0}$

First order energy: $E_0^1 = \left\langle 0\middle|\tilde{W}\middle|0\right\rangle = 0$

Second order energy: $E_0^2 = \sum_{n\neq 0} \frac{\left\langle 0\middle|\tilde{W}\middle|n\right\rangle\left\langle n\middle|\tilde{W}\middle|0\right\rangle}{E_0 - E_n}$

Your textbook uses several approximations to estimate

$$-\frac{8k_e e^2 a_0^5}{a^6} \leq E_0^2 \leq -\frac{8k_e e^2 a_0^5}{a^6}\left(\frac{8}{9}\right)^{10}$$

HW #5 involves examining this result

Generalization of this result concludes that the dominant interaction of two induced dipoles at distance R takes the form:

$$W_{\text{VdW}} = -\frac{A}{R^6}$$

Now consider the effects of a uniform magnetic field on atom which has angular momentum and spin --

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

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

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

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

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

Detail:

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

Vector potential $\mathbf{A} = \frac{1}{2}\mathbf{r}\times\mathbf{B}$

$$\mu_B = \frac{e\hbar}{2mc}$$

$$|g| = 2.00231930436182$$

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

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

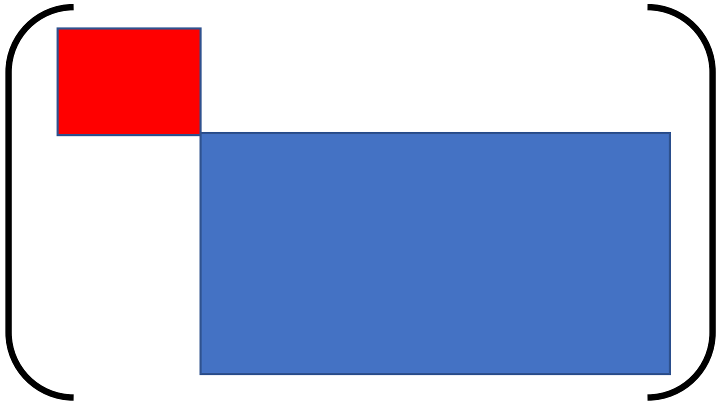
$$H^0 = \frac{\mathbf{p}^2}{2m} + V(r)$$

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

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

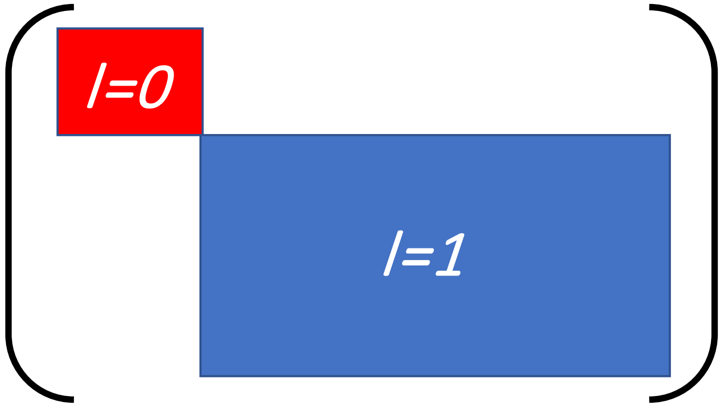
$\Rightarrow 8\times 8$ perturbation matrix:

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



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

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



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

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

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

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

$$J_\pm|jm\rangle = \hbar\sqrt{j^2-m^2+j\mp m}\,|j(m\pm1)\rangle$$

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

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

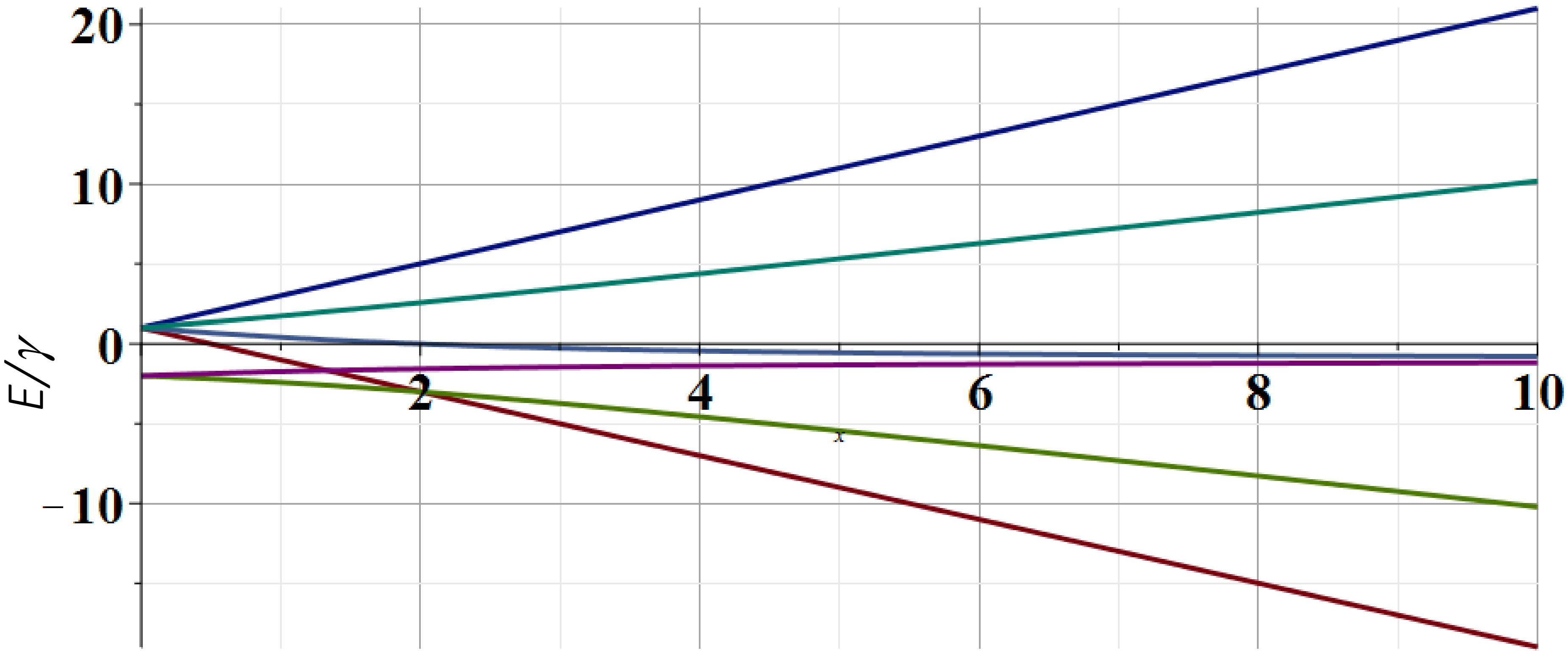
$$\beta \equiv \mu_B \mathrm{B}_0$$

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

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

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

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



Now consider internal magnetic fields within an atom

In PHY 712 we will derive the famous hyperfine interaction potential --

$$\mathbf{B}_{\boldsymbol{\mu}_e}(\mathbf{r}) = \frac{\mu_0}{4\pi}\left(\frac{3\hat{\mathbf{r}}\left(\boldsymbol{\mu}_e \cdot \hat{\mathbf{r}}\right) - \boldsymbol{\mu}_e}{r^3} + \frac{8\pi}{3}\boldsymbol{\mu}_e \delta(\mathbf{r})\right)$$

Magnetic field near nucleus due to orbiting electron:

$$\mathbf{B}_O(\mathbf{r}) = \frac{\mu_0}{4\pi}\frac{e}{m_e} L_z \hat{\mathbf{z}} \left\langle \frac{1}{r^3} \right\rangle$$

"Hyperfine" interaction energy:

$$\mathcal{H}_{HF} = -\boldsymbol{\mu}_N \cdot \left(\mathbf{B}_{\boldsymbol{\mu}_e}(\mathbf{r}) + \mathbf{B}_O(\mathbf{r})\right)$$

$$= \frac{\mu_0}{4\pi}\left(\frac{3\left(\boldsymbol{\mu}_N \cdot \hat{\mathbf{r}}\right)\left(\boldsymbol{\mu}_e \cdot \hat{\mathbf{r}}\right) - \boldsymbol{\mu}_N \cdot \boldsymbol{\mu}_e}{r^3} + \frac{8\pi}{3}\boldsymbol{\mu}_N \cdot \boldsymbol{\mu}_e \delta(\mathbf{r}) + \frac{e}{m_e}\left\langle \frac{\mathbf{L} \cdot \boldsymbol{\mu}_N}{r^3} \right\rangle\right)$$