

- Finish a few odds and ends from previous lectures.

(1) Brillouin-Wigner form of the perturbation theory expansion.

(2) The Van der Waals force from perturbation theory ( $H_1 \approx T_{m=0}^{\ell=2}$ ).

(3)  $Z_{eff}$  as a parameter (corresponding to the protons being screened by the electron cloud) and minimizing in  $Z_{eff}$ .  $\langle \vec{x}_1 \vec{x}_2 | \tilde{0} \rangle = (Z_{eff}^3 / \pi a_0^3) e^{-Z_{eff}(r_1+r_2)/a_0}$  leads to  $E_{trial} = \langle \tilde{0} | H | \tilde{0} \rangle = (Z_{eff}^2 - 2ZZ_{eff} + \frac{5}{8}Z_{eff}^2)(e^2/a_0)$ . Minimization gives  $Z_{eff} = 2 - (5/16) \approx 1.69 < 2$ . Then  $E_{trial} = -77.5\text{eV}$

(4) Consider an excited state where one of the electrons is in the  $1s$  groundstate and the other is in an  $n\ell$  excited state. If the spins are in the antisymmetric singlet state, we symmetrize in the spatial wavefunction, and if in the spin triplet state we antisymmetrize. Find for the first order perturbation  $\langle e^2/r_{12} \rangle = I \pm J$ , where  $I = \int d^3\vec{x}_1 \int d^3\vec{x}_2 |\psi_{100}(\vec{x}_1)|^2 |\psi_{n\ell m}(\vec{x}_2)|^2 e^2/r_{12}$  is the *direct* term and  $J$  is the *exchange* integral. It turns out that  $J > 0$  so the spin singlet has higher energy than the triplet. The singlet states were named parahelium and the triplet were named orthohelium.

- Let's consider an example of an  $H(t)$  that can be solved exactly (Rabi). Two state system with  $H = H_0 + H_t(t)$  and  $H_0 = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2|$  and  $H_1 = \gamma e^{i\omega t}|1\rangle\langle 2| + h.c.$ . Suppose  $|\psi(t_0 = 0)\rangle = |1\rangle$ . Find the probability of finding the system in state  $|2\rangle$  at a later time  $t$  as given by Rabi's formula:

$$|c_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega - \omega_{21})^2/4} \sin^2 \Omega t,$$

where  $\omega_{21} \equiv (E_2 - E_1)/\hbar$  and  $\Omega \equiv \sqrt{(\gamma^2/\hbar^2) + \frac{1}{4}(\omega - \omega_{21})^2}$ . Resonant enhancement of the transition amplitude when  $\omega \approx \omega_{21}$ . Of course  $|c_1(t)|^2 = 1 - |c_2(t)|^2$ . The times of growing  $|c_2(t)|^2$  are absorption and those of decreasing  $|c_2(t)|^2$  are emission.

Example spin magnetic resonance:  $\vec{\mu} = e\vec{S}/m_e c$  in  $\vec{B} = B_0\hat{z} + B_1(\hat{x}\cos\omega t + \hat{y}\sin\omega t)$ . Identify  $\omega_{21} = |e|B_0/m_e c$  and  $\gamma = |e|\hbar B_1/2m_e c$ .