

- Recall the original way we obtained the perturbation theory expressions:  $(H_0 + H_1)|E_n\rangle = E_n|E_n\rangle$  and we expand  $E_n = \sum_{L=0} E_n^{(L)}$  and  $|E_n\rangle = \sum_L |E_n^{(L)}\rangle$ , where the superscript is the power of  $\epsilon \sim H_1/H_0$ . Project on  $\langle E_n^{(0)}|$  and take  $\langle E_n^{(0)}|E_n\rangle = 1$  and  $\langle E_n|E_n\rangle \equiv Z_n^{-1}$ , as in the last lecture. So get the exact relation (all orders in  $\epsilon$ )

$$E_n = E_n^{(0)} + \langle E_n^{(0)}|H_1|E_n\rangle, \quad \text{i.e.} \quad E_n^{L>0} = \langle E_n^{(0)}|H_1|E_n^{(L-1)}\rangle.$$

Likewise, project  $(H_0 + H_1)|E_n\rangle = E_n|E_n\rangle$  on  $\langle m^{(0)}|$  to get

$$|E_n\rangle = |E_n^{(0)}\rangle + \sum_m' |E_m^{(0)}\rangle \frac{1}{E_n - E_m^{(0)}} \langle E_m^{(0)}|H_1|E_n\rangle.$$

Note that this is a slightly different packaging of the perturbative expansion as compared with before: it is the full, all orders  $E_n$  in the denominator, and in  $|E_n\rangle$ . This is the starting point of Brillouin-Wigner perturbation theory (discussed in e.g. Baym). It can be unpacked a bit by iterating the expression for  $|E_n\rangle$  in terms of its perturbative expansion on the RHS. The results are non-linear equations for  $E_n$ , and expanding around known approximate solutions, not necessarily  $E_n^{(0)}$  can lead to improved convergence vs the standard (Rayleigh Schrodinger) perturbative expansion.

- Variational method: show that the functional

$$E[|\psi\rangle] \equiv \frac{\langle \psi|H|\psi\rangle}{\langle \psi|\psi\rangle} \geq E_0,$$

with equality iff  $|\psi\rangle$  is the groundstate. Can use this to bound and estimate the groundstate energy by guessing and scanning over various trial states. And the lowest value of the LHS is the state closest to the actual groundstate.

Also for excited states, it is a theorem that the functional  $E[|\psi\rangle]$  on the Hilbert space is stationary for precisely the discrete energy eigenstates, and the stationary values are the discrete energy eigenvalues. Proof: vary  $\delta E$  from the definition, and show that the condition  $\delta E = 0$  requires  $\langle \delta\psi|(H - E)|\psi\rangle = 0$ .

Example: estimate the groundstate energy of the 1d particle in a box,  $|x| \leq a$  by trial functions that satisfy  $\psi(-x) = \psi(x)$  and  $\psi(a) = 0$ . E.g.  $\psi = |a|^\lambda - |x|^\lambda$  and then find  $E_{trial}(\lambda) = (\lambda + 1)(2\lambda + 1)(2\lambda - 1)^{-1}(\hbar^2/4m^2a^2)$  and minimize in  $\lambda$  to get  $E_{trial} = (5 + 2\sqrt{6})\pi^{-2}E_0 = 1.00298E_0$ .

- Example: Coulomb potential:  $H = \vec{p}^2/2m - Ze^2/r$ . We know the answer, but use it to illustrate the variational method. Try  $\psi(r) = Ce^{-\lambda r}$  (this is the right choice; one could also try wrong things like  $\psi_{trial}(r) = e^{-\lambda r^2}$  and get pretty good results). Find

$$E_{trial}(\lambda) = \int_0^\infty dr r^2 e^{-\lambda r} \left( -\frac{\hbar^2}{2mr^2} \frac{d}{dr} (r^2 \frac{d}{dr} e^{-\lambda r}) - \frac{Ze^2}{r} e^{-\lambda r} \right) / \int_0^\infty dr r^2 e^{-2\lambda r}.$$

Verify that minimizing w.r.t.  $\lambda$  gives the correct groundstate wavefunction and energy.

- Groundstate of Helium. First try treating electron-electron term as a perturbation. The 0th order result is then that of two essentially decoupled Coulomb potential systems, where we must impose Fermi statistics. So put the two electron spins in the singlet, and the orbital part is  $\psi_{1,0,0}(\vec{x}_1)\psi_{1,0,0}(\vec{x}_2) = (Z^3/\pi a_0^3)e^{-Z(r_1+r_2)/a_0}$ , where  $Z = 2$  for He, and  $E_0^{(0)} = 2 \times Z^2 \times (-e^2/2a_0)$ . The first order correction is  $\langle (e^2/r_{12}) \rangle$ . This is computed by expanding  $1/r_{12} = \sum_{\ell=0}^\infty \frac{r_{<}^\ell}{r_{>}^{\ell+1}} P_\ell(\cos \gamma)$  and  $P_\ell(\cos \gamma) = \frac{4}{2\ell+1} \sum_{m=-\ell}^\ell Y_{\ell,m}^*(\theta_1, \phi_1) Y_{\ell,m}(\theta_2, \phi_2)$ . The final result is  $E_0^{(1)} = (5/2)(e^2/2a_0)(Z/2)$ . This gives  $E_0^{(0)} + E_0^{(1)} \approx (-8 + \frac{5}{2})(e^2/2a_0) \approx -74.8eV$  vs  $E_{exp} = -78.8eV$ . Pretty good! Can do even better by treating  $Z_{eff}$  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  $E_{trial} = \langle \tilde{0} | H | \tilde{0} \rangle = (Z_{eff}^2 - 2ZZ_{eff} + \frac{5}{8}Z_{eff}^3)(e^2/a_0)$ . Minimization gives  $Z_{eff} = 2 - (5/16) \approx 1.69 < 2$ . Then  $E_{trial} = -77.5$ .

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.