1/24/08

Now a perturbation analysis of He. Take

$$H_0 = \left(\frac{p_1^2}{2} - \frac{Z}{r_1}\right) + \left(\frac{p_2^2}{2} - \frac{Z}{r_2}\right)$$

$$H_1 = \frac{1}{r_{12}}$$

This is not very favorable for perturbation theory, since H_1 is not particularly small compared to H_0, but we do it anyway because there is not much choice. First look at eigenstates, -values of unpert. system. Eigenfunctions are products of two hydrogen-like central force wavefns (spatial part only), what we will write as

$$|n_1 l_1 m_1\rangle^{(1)} \, |n_2 l_2 m_2\rangle^{(2)} \equiv |n_1 l_1 m_1 \, n_2 l_2 m_2\rangle.$$

The unperturbed energies are specified by the 2 principal qu. #'s n_1, n_2,

means 0th order in pert'n th.

$$E^{(0)}_{n_1 n_2} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right).$$

The eigenstates above are not eigenstates of E_{12}^{orb} (not symmetrized). When we symmetrize them, there are 2 cases:

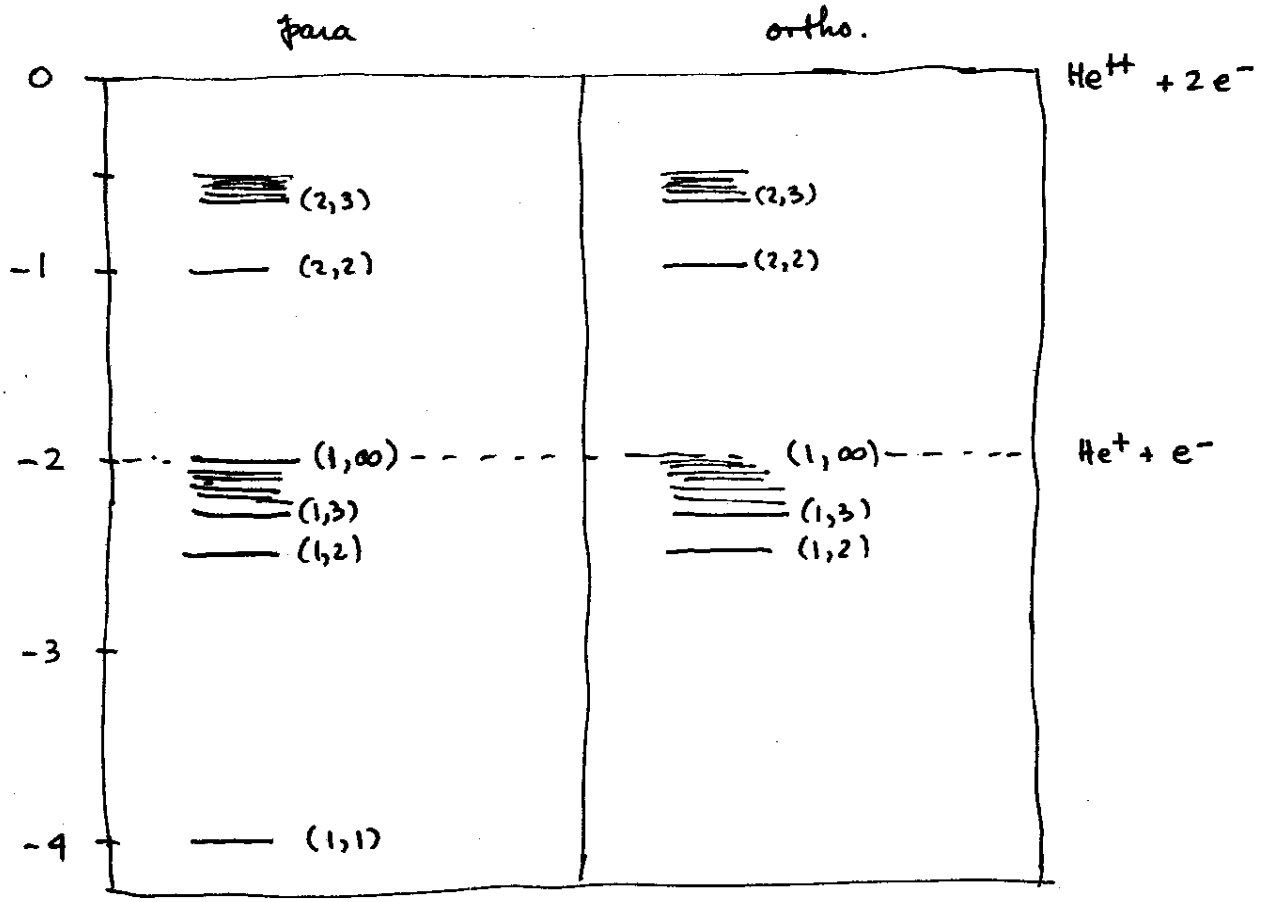
<u>Case I:</u> $(n_1 l_1 m_1) = (n_2 l_2 m_2) \equiv (nlm)$.

State $|nlm\,nlm\rangle$ is a para state.
No ortho state exists in this case

<u>Case II</u> $(n_1 l_1 m_1) \neq (n_2 l_2 m_2)$.

$$\text{Symm. state} = \frac{1}{\sqrt{2}}\left[|n_1 l_1 m_1 \, n_2 l_2 m_2\rangle \pm |n_2 l_2 m_2 \, n_1 l_1 m_1\rangle\right] \quad \begin{array}{l} + = \text{para} \\ - = \text{ortho.} \end{array}$$

The symmetrization (or antisymm.) does not affect the energy $E^{(0)}_{n_1 n_2}$. We make an energy level diagram for H_0. (for helium, $Z=2$). Shown are eigenstates by quantum numbers (n_1, n_2).



Interesting to compare this with exact helium level diagram. The ground state is correctly on the singlet (para) side, but it is rather much too low (−4.0 vs −2.9). In fact, all the states are too low, to be expected since H_1 is a positive operator. (The electron repulsion causes the unperturbed wave functions to expand away from the nucleus, and ~~to lowers~~ raises the energy.) The unperturbed energies are degenerate in l_1, l_2 (because H-like) so there is no staircase effect and no attempt in diagram above to resolve levels by L value. There

is also no difference between ortho and para energies for same (n_1, n_2), unlike in true helium. But we can see why there is no 1^3S state in real helium: this would be a $(1,1)$ state with odd spatial symmetry, something that is impossible since $|100\rangle$ is nondegen. in H.

Notice that all the bound states have $n_1 = 1$, with $n_2 = 1, 2, 3, \ldots \infty$. These are <u>singly excited states</u>. There are also states with both $n_1, n_2 > 1$, the <u>doubly excited states</u>, but they all lie above the continuum limit $E = -2$. The sequence $n_1 = 2$, $n_2 = 2, 3, \ldots, \infty$ is shown in the figure. These are examples of <u>discrete states imbedded in the continuum</u>. When the perturbation $1/r_{12}$ is turned on, they become <u>resonances</u>. They are not genuine bound states of real helium.

Now consider the qualitative effects of the perturbation. First, it raises the energies of all states (already noted). Second, it raises para states more than ortho states, because a para state is spatially symm., thus $\psi(\vec{r}_1, \vec{r}_2)$ has a maximum at $\vec{r}_1 = \vec{r}_2$ while for an ortho state, $\psi = 0$ at $\vec{r}_1 = \vec{r}_2$. Since $1/r_{12} \to \infty$ when $\vec{r}_1 = \vec{r}_2$, the energy is raised more for para states. Finally, the perturbation will lift the L-degeneracy, which was accidental in H anyway.

To be more quantitative, compute ΔE by 1st order pert'n th. 1/24/08 for ground state.

$$\Delta E = \langle 100\,100 | \frac{1}{r_{12}} | 100\,100 \rangle, \qquad \psi_{100}(\vec{r}) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}$$

$$= \int d^3\vec{r}_1\, d^3\vec{r}_2 \; \frac{|\psi_{100}(\vec{r}_1)|^2\, |\psi_{100}(\vec{r}_2)|^2}{r_{12}}.$$

This has an electrostatic interpretation: It is the electrostatic energy of interaction of two overlapping electron clouds, each given by $|\psi_{100}|^2$. To evaluate, use formula for $\psi_{100}(\vec{r})$, expand Coulomb denominator in series of Legendre polynomials,

$$\frac{1}{r_{12}} = \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{l=0}^{\infty} \frac{r_<^{\,l}}{r_>^{\,l+1}} \underbrace{P_l(\hat{r}_1 \cdot \hat{r}_2)}$$

$$= \frac{4\pi}{2l+1} \sum_m Y_{lm}^*(\Omega_1)\, Y_{lm}(\Omega_2).$$

So,

$$\Delta E = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2\, d\Omega_1 d\Omega_2 \left(\frac{Z^6}{\pi^2}\right) e^{-2Z(r_1+r_2)}$$

$$\sum_{lm} \frac{4\pi}{2l+1} \frac{r_<^{\,l}}{r_>^{\,l+1}} Y_{lm}^*(\Omega_1)\, Y_{lm}(\Omega_2).$$

insert $1 = \sqrt{4\pi}\, Y_{00}^*(\Omega_2)$

Do Ω_2 integral first, $\int d\Omega_2\, Y_{lm}(\Omega_2) = \sqrt{4\pi}\, \delta_{l0}\, \delta_{m0}$

1/24/08

so,

$$\Delta E = \frac{Z^6}{\pi^2} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int d\Omega_1 \; e^{-2Z(r_1+r_2)} \cdot (4\pi) \frac{1}{r_>} Y_{00}^*(\Omega_1) \sqrt{4\pi}$$

$$= 16 Z^6 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \; \frac{e^{-2Z(r_1+r_2)}}{r_>}$$

$$= 16 Z^6 \left[\int_0^\infty r_1^2 dr_1 \, e^{-2Zr_1} \int_{r_1}^\infty r_2^2 dr_2 \; \frac{e^{-2Zr_2}}{r_2} \right. \qquad (\text{term } r_1 < r_2)$$

$$\left. + \int_0^\infty r_1^2 dr_1 \; \frac{e^{-2Zr_1}}{r_1} \int_0^{r_1} r_2^2 dr_2 \; e^{-2Zr_2} \right] \qquad (\text{term } r_1 > r_2)$$

$$= \frac{5}{8} Z \qquad \text{when smoke clears.}$$

So, to 1st order,

1st order pertn th.

$$E_{gnd}^{(1)} = -Z^2 + \frac{5}{8} Z.$$

Table:

Z	$E_{gnd}^{(0)}$	$E_{gnd}^{(1)}$	E_{gnd}^{exact}
2	-4	-2.75	-2.904
1	-1	-0.375	-0.528

1/24/08

The correction brings us much closer to the true energy, but it has overshot the mark. In the case of H^-, the corrected energy is above the continuum limit. This gives us no information about the existence of H^- as a bound state (assuming we did not know it existed), because perturbation estimates can be either high or low, and we do not have any error bounds. (The variational method works better in this regard.)