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Now excited states of He. As before, $H = H_0 + H_1$, where

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

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

First understand the unperturbed system. H_0 is the sum of two identical H-like single particle Hamiltonians, one for each electron.

Let the single particle eigenfunctions (spatial part only) be $|n, l, m\rangle$ (usual central force quantum numbers). Then the eigenfunctions of H_0 can be written

$$|n_1, l_1, m_1\rangle |n_2, l_2, m_2\rangle \equiv |n_1, l_1, m_1, n_2, l_2, m_2\rangle$$

giving the single particle H-like quantum numbers for electrons 1 and 2. This is ket language for

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_{n_1, l_1, m_1}(\vec{r}_1) \psi_{n_2, l_2, m_2}(\vec{r}_2)$$

(spatial part only). The unperturbed energy of this state is

$$E_{n_1 n_2}^{(0)} = -\frac{Z^2}{2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \quad (\text{indep of } l_1, m_1, l_2, m_2).$$

Here (0) means, 0th order of perturbation theory.

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(just sum of two H-like energies).

These eigenfns are eigenfns of H_0 , but not of E_{12}^{orb} .

By forming linear combs we make simultaneous eigenfns of H_0 and E_{12}^{orb} (a symmetry adapted basis). There are 2 cases:

Case I, $(n_1, l_1, m_1) = (n_2, l_2, m_2) \equiv (nlm)$.

State $|nlm, nlm\rangle$ is automatically + under E_{12}^{orb} : it is a para state.

Case II, $(n_1, l_1, m_1) \neq (n_2, l_2, m_2)$. State

$$\frac{1}{\sqrt{2}} [|n_1, l_1, m_1, n_2, l_2, m_2\rangle \pm |n_2, l_2, m_2, n_1, l_1, m_1\rangle]$$

is eigenstate of H_0 and E_{12}^{orb} , + = para, - = ortho state.

Terminology: An orbital is a single particle wave fn, for example, $|n_1, l_1, m_1\rangle$ or $|n_2, l_2, m_2\rangle$ above are H-like orbitals.

Above we are creating multiparticle states as (tensor) products of single particle orbitals, then symmetrizing or anti-symmetrizing to make eigenstates of E_{12}^{orb} . For such states we can speak of the single particle state that each electron is "in". Thus we say, electron 1 is in the state

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n_1, l_1, m_{l1} , and electron 2 in state n_2, l_2, m_{l2} . Often we use spectroscopic notation, ignoring m qu. numbers, and say, for example, electron 1 is in state $1s$ and electron 2 in state $2p$. In such a case we would say that the electron configuration is $1s2p$. In general, the elec. config. is just a list of single particle qu. numbers of the states that the single electrons are in. Here are some configurations for He:

$1s^2$	both elec's in gnd state
$1s2s$	}
$1s2p$	
$1s3s$	
\vdots	
$2s^2$	}
$2s2p$	
$2s3d$	
\vdots	

Notice, however, that such terminology is rigorously speaking only meaningful when the 2-particle state is a product of single particle orbitals. In general, 2-particle states cannot be written as products of single particle orbitals, although they can always be written as sums of such products. See sec. ~~11.2~~ ^{15.2 and 25.3} of the notes. Although the eigenstates of H_0 are products of single particle

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orbitals, those of $H_0 + H_1$, are not. Thus, for example, the notion of the electron configuration for the exact ground state of He, or the exact ground state of $H_0 + H_1$, (which are not quite the same thing) will have to be clarified. The proper definition of electron configuration in those cases involves Hartree-Fock theory.

We now consider perturbation theory for the excited states of He. We only consider the singly excited states, because the doubly excited states all lie above the continuum threshold at $E = -2$ a.u., even before H_1 is turned on. H_1 is a positive operator and can only raise the energies, so the doubly excited states of H_0 have no hope of being bound states after we switch on H_1 .

The singly excited states of H_0 all have the form

$$|NLM_L \pm\rangle = \frac{1}{\sqrt{2}} (|100nlm\rangle \pm |nlm100\rangle)$$

where

$$N = n$$

$$L = l$$

$$M_L = m$$

We use capital letters for the qu. #'s

of the whole atom, and lower case for

those of single electrons (the usual convention). In this case the values are the same, because the electron in the ground state

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100 has $l=0$, so all the angular momentum comes from the electron in the excited state nlm , so $L=l$ and $M_L=m$. As for N , it is just an energy sequencing number. Whether we use NLM_L or nlm just depends on which aspect we want to emphasize. The \pm in $|NLM_L \pm\rangle$ is the spatial exchange symmetry (e_{12}^{orb}), i.e., ortho = -, para = +.

The unperturbed energy of $|NLM_L \pm\rangle$ is

$$E_N^{(0)} = -\frac{Z^2}{2} \left(1 + \frac{1}{N^2}\right) \quad (n_1=1, n_2=N=n).$$

so it is indep. of $LM_L \pm$, and we have degeneracy in these qu. #'s.

But the corresponding operators L^2, L_z, E_{12}^{orb} all commute w. H_1 , so there is no matrix to diagonalize in 1st order degen. pert. th., and the energy shifts are just the diagonal elements. Thus:

$$\begin{aligned} \Delta E &= \langle NLM_L \pm | H_1 | NLM_L \pm \rangle \\ &= \frac{1}{2} \left(\langle 100 nlm | \frac{1}{r_{12}} | 100 nlm \rangle + \langle nlm 100 | \frac{1}{r_{12}} | nlm 100 \rangle \right) \\ &\pm \frac{1}{2} \left(\langle 100 nlm | \frac{1}{r_{12}} | nlm 100 \rangle + \langle nlm 100 | \frac{1}{r_{12}} | 100 nlm \rangle \right). \end{aligned}$$

Both pairs of matrix elements in the parens are equal, so

$$\Delta E = J_{nl} \pm K_{nl}, \quad \text{where}$$

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$$\begin{aligned}
 J_{ne} &= \langle 100 nlm | \frac{1}{r_{12}} | 100 nlm \rangle \\
 &= \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{|\psi_{100}(\vec{r}_1)|^2 |\psi_{nlm}(\vec{r}_2)|^2}{r_{12}} = \text{direct integral.}
 \end{aligned}$$

$$\begin{aligned}
 K_{ne} &= \langle 100 nlm | \frac{1}{r_{12}} | nlm 100 \rangle \\
 &= \int d^3\vec{r}_1 d^3\vec{r}_2 \psi_{100}^*(\vec{r}_1) \psi_{nlm}^*(\vec{r}_2) \frac{1}{r_{12}} \psi_{nlm}(\vec{r}_1) \psi_{100}(\vec{r}_2) \\
 &= \text{exchange integral.}
 \end{aligned}$$

Notice $J_{ne} > 0$ always. K_{ne} is also > 0 ; I know no proof of this, but the integrand in the 6D space is dominated by regions where $\vec{r}_1 \approx \vec{r}_2$ ~~so that~~ ^{where} r_{12} is small, and in such regions the product of the four wavefns is approx. $|\psi_{100}(\vec{r})|^2 |\psi_{nlm}(\vec{r})|^2$ where $\vec{r} = \vec{r}_1 \approx \vec{r}_2$. The point is that the integrand is positive in such regions.

The term $\pm K_{ne}$ shows that H_1 removes the degeneracy of H_0 in the \pm sign (exchange degeneracy), causing the ortho states (-) to be lower in energy than the para states (+). See fig ^{25.3} ~~25.3~~. This explains an important qualitative feature of the exact spectrum

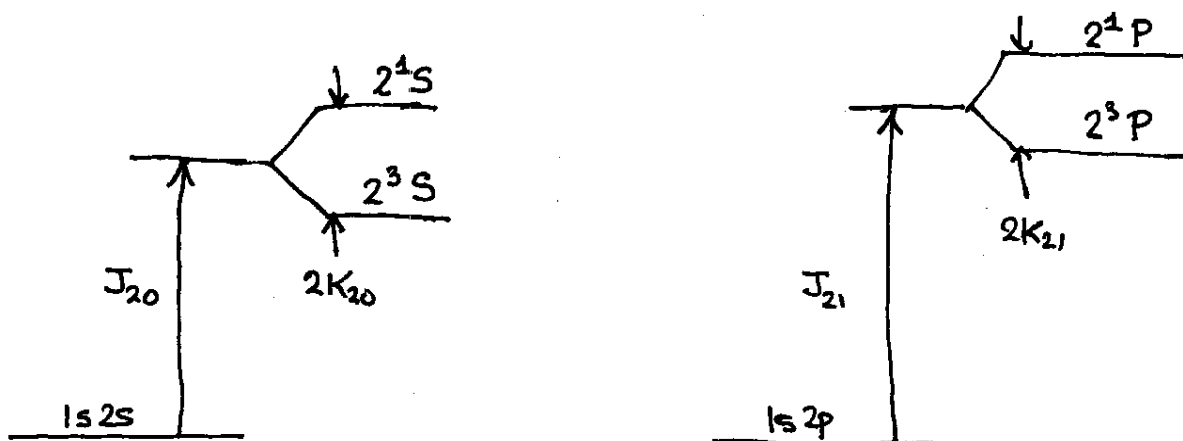
of He.

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The direct integral has a simple interpretation as the mutual electrostatic energy of interaction of the two electron clouds $|\psi_{100}|^2$ and $|\psi_{n\ell m}|^2$. It is physically reasonable that the exact energy would contain such a contribution. When we did the perturbation analysis of the ground state of He, the direct integral was all we had (with $n\ell m = 100$). There was no exchange integral. For the excited states, however, there is also the exchange integral.

The exchange integral does not have such a simple electrostatic interpretation. It actually involves non-classical correlations of the two electrons in the 6D config space.

If we look at the $n=2$ excited states, we get perturbation theory estimates for the energies of the 2^1S , 2^1P , 2^3S and 2^3P states:



The direct integrals $J_{n\ell}$ are an increasing fn. of ℓ , which lies behind the staircase effect; the physics of this is the fact

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that larger l means the wave fn. for the outer electron is at a larger radius, hence more effectively screened by inner electron. This is the same explanation as in the alkalis.

We see that perturbation theory can explain all the qualitative features of the excited states of He. It is not too good, however, quantitatively, at least as we have been using it, because the perturbation $1/r_{12}$ is not particularly small, and H_0 is not a very good approximation to $H = H_0 + H_1$.

Better results are obtained, at least for the ground state, by using the variational method. First write out the ground state wave fn (config $1s^2$) of H_0 used above:

$$\Psi_{1s^2}(\vec{r}_1, \vec{r}_2) = \frac{z^3}{\pi} e^{-z(r_1 + r_2)}$$

It is just the product of 2 H-like ground state wave fns. The unpert. energy (-4) is rather badly off. Physically what is wrong with this is that the electrons repel one another, so the electron cloud wants to expand somewhat away from the nucleus. Equivalently, we may say that each electron partially screens the other from the full nuclear charge, so each sees a somewhat

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reduced effective nuclear charge, call it $Z_e = Z_{\text{effective}}$. 1/29/08

This suggests a trial wave fn. for the variational method, gnd state

$$\psi_{\text{trial}}(\vec{r}_1, \vec{r}_2) = \frac{Z_e^3}{\pi} e^{-Z_e(r_1 + r_2)}$$

It is the product of two H-like gnd states, with an effec. nuclear charge.

We regard Z_e as a variational parameter; we find the best choice of Z_e by minimizing $\langle \psi_{\text{trial}} | H | \psi_{\text{trial}} \rangle$ wr.t. Z_e .

This is an example of how use physical reasoning to choose a trial wave fn.

The expectation value we need is

$$\langle \psi | \left(\frac{p_1^2}{2} - \frac{Z_e}{r_1} \right) + \left(\frac{p_2^2}{2} - \frac{Z_e}{r_2} \right) + (Z_e - Z) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} | \psi \rangle$$

where $|\psi\rangle = |\psi_{\text{trial}}\rangle$. We have written H in terms of two H-like Hamiltonians with charge Z_e , then added correction terms (proportional to $Z_e - Z$) to make the potential Z/r as it must be in the true H .

The expectation val. of the 1st term $\frac{p_1^2}{2} - \frac{Z_e}{r_1}$ is easy. The coords of particle 2 integrate out to give 1, since this operator only depends on the coords of particle 1. The result is a single particle expectation value, of a H-like Hamiltonian wr.t. its own ground state. The result is just $-\frac{Z_e^2}{2}$, the gnd state energy.

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The 2nd term gives the same answer (just mult by 2).

As for the term $(z_e - z) \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$, ~~there~~ it gives $2 \times (z_e - z)$ times the single particle expect. val. of $\frac{1}{r}$, which is z_e (see Eq. (21.25)). So this term gives

$$2(z_e - z)z_e.$$

The last term $\frac{1}{r_{12}}$ gives an expect. val. that can be evaluated just like we did in the pert'n treatment of the ground state (see notes for 1/24/08, p. 5) but with z_e instead of z .

The answer is $5/8 z_e$. Altogether,

$$\begin{aligned} F(z_e) &= \langle \psi | H | \psi \rangle = 2 \left(-\frac{z_e^2}{2} \right) + 2(z_e - z)z_e + \frac{5}{8}z_e \\ &= z_e^2 - 2zz_e + \frac{5}{8}z_e. \end{aligned}$$

The wave fns ψ_{trial} are normalized for all values of z_e , so we don't need any Lagrange multipliers to enforce normalization.

To minimize $F(z_e)$, just use calculus:

$$\frac{\partial F}{\partial z_e} = 2z_e - 2z + \frac{5}{8} = 0 \Rightarrow \boxed{z_e = z - 5/16}$$

We see that each electron screens $5/16$ of a nuclear charge from the other electron. When we evaluate $F(z_e)$ at this

value of Z_e , we get the variational estimate of the ground state energy: (11)
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$$F\left(Z - \frac{5}{16}\right) = -Z^2 + \frac{5}{8}Z - \frac{25}{256}.$$

The answer is the same as the results of 1st order perturbation theory, minus the const $\frac{25}{256}$. Since the variational method gives an upper bound to the ground state energy, we see that ~~the~~ 1st order perturbation theory gave an answer that was too high, but the variational method corrects it somewhat.

Here is a table of actual numbers:

Atom	Z	Z_{eff}	$E_{\text{gnd}}^{(0)}$	$E_{\text{gnd}}^{(1)}$	$E_{\text{gnd}}^{\text{var}}$	$E_{\text{gnd}}^{\text{exact}}$
H^-	1	$1\frac{1}{16}$	-1	-0.375	-0.473	-0.528
He	2	$1\frac{1}{16}$	-4	-2.75	-2.848	-2.904

order of pertn th.
↓

(all in a.u.)

For He, the var. method gives an energy that is only 0.056 au off. For H^- , the variational energy is still above the continuum limit (-0.5), so the calculation has not succeeded in proving the existence of a bound state. For that it is necessary to use a more complicated trial wave fn, one which incorporates the fact that the two electrons like to stay on opposite sides of

the nucleus (thus, the electrons are correlated).

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