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

$$|n_1 l_1 m_1\rangle |n_2 l_2 m_2\rangle = |n_1 l_1 m_1 n_2 l_2 m_2\rangle$$

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

$$\Psi(r_1, r_2) = \psi_{n_1, l_1, m_1}(r_1) \psi_{n_2, l_2, m_2}(r_2)$$

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

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

Here $(0)$ means, $0^{\text{th}}$ order of perturbation theory.
(just sum of two H-like energies).

These eigenfns are eigenfns of $H_0$, but not of $E_{12}^{\text{orb}}$. By forming linear combos we make simultaneous eigenfns of $H_0$ and $E_{12}^{\text{orb}}$ (a symmetry adapted basis). There are 2 cases:

Case I, $(n_1 l_1 m_1) = (n_2 l_2 m_2) = (n l m)$.

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

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

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

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

---

Terminology: An orbital is a single particle wave fn, for example, $|n l m_1\rangle$ 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 $E_{12}^{\text{orb}}$. 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
\( n_1, l_{1M_1}, \text{ and electron 2 in state } n_2, l_{2M_2}. \) 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 electron configuration is just a list of single particle qu. numbers of the states that the single electrons are in. Here are some configurations for He:

\[
\begin{align*}
1s^2 & \quad \text{both electrons in ground state} \\
1s2s & \\
1s2p & \quad \text{singly excited states} \\
1s3s & \\
2s^2 & \\
2s2p & \quad \text{doubly excited states} \\
2s3d & \\
\end{align*}
\]

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. 104 of the notes. Although the eigenstates of \( H_0 \) are products of single particle
orbitals, those of $Ho + H$, are not. Thus, for example, the
motion of the electron configuration for the exact ground
state of He, or the exact ground state of $Ho + H$, (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 $H_i$ is
turned on. $H_i$ is a positive operator and can only
raise the energies, so the doubly excited states of $Ho$ have
no hope of being bound states after we switch on $H_i$.

The singly excited states of $Ho$ all have the form

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

where $N=n$, $L=l$, $M_{L} = m$ 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
has \( l=0 \), so all the angular momentum comes from the 
electron in the excited state \( nlm \), so \( l=2 \) 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

\[
E^{(0)}_N = - \frac{Z^2}{2} \left( 1 + \frac{1}{N^2} \right) \quad (n_1=1, \; n_2=N=n),
\]

so it is indep. of \( LLM_L \), and we have degeneracy in these \( q \nu \) #1's.

But the corresponding operators \( L^2, L_L, E_{12}^{orb} \) all commute w. \( H_1 \), so

there is no matrix to diagonalize in 1st order degen. pert. \( H_1 \), and

the energy shifts are just the diagonal elements. Thus:

\[
\Delta E = \langle NLM_L \pm | H_1 | NLM_L \pm \rangle
\]

\[
= \frac{1}{2} \left( \langle 100 nlm | \frac{1}{n_2} | 100 nlm \rangle + \langle nlm 100 | \frac{1}{n_2} | nlm 100 \rangle \right)
\]

\[
\pm \frac{1}{2} \left( \langle 100 nlm | \frac{1}{n_2} | nlm 100 \rangle + \langle nlm 100 | \frac{1}{n_2} | 100 nlm \rangle \right).
\]

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

\[
\Delta E = T_{nl \pm} K_{nl}, \quad \text{where}
\]
\[ J_{nl} = \langle 100 \text{ nlm} \mid \frac{1}{r_{12}} \mid 100 \text{ nlm} \rangle \]

\[ = \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{|\psi_{100}(\vec{r}_1)|^2 |\psi_{n0m}(\vec{r}_2)|^2}{r_{12}} = \text{direct integral.} \]

\[ K_{nl} = \langle 100 \text{ nlm} \mid \frac{1}{r_{12}} \mid \text{nlm} 100 \rangle \]

\[ = \int d^3\vec{r}_1 d^3\vec{r}_2 \psi_{100}^*(\vec{r}_1) \psi_{n0m}^*(\vec{r}_2) \frac{1}{r_{12}} \psi_{n0m}(\vec{r}_1) \psi_{100}(\vec{r}_2) \]

\[ = \text{exchange integral.} \]

Notice \( J_{nl} > 0 \) always. \( K_{nl} \) is also \( > 0 \); I know no proof of this, but the integrand in the 6D space is dominated by regions where \( \vec{r}_1 \approx \vec{r}_2 \) and \( r_{12} \) is small, and in such regions the product of the four wavefns is approx. \( |\psi_{100}(\vec{r})|^2 |\psi_{n0m}(\vec{r})|^2 \) where \( \vec{r} = \vec{r}_1 \approx \vec{r}_2 \). The point is that the integrand is positive in such regions.

The term \( \pm K_{nl} \) 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. This explains an important qualitative feature of the exact spectrum.
of He.

The direct integral has a simple interpretation as the mutual electrostatic energy of interaction of the two electron clouds \( |\Psi_{100}\|^2 \) and \( |\Psi_{20}\|^2 \). 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 \( nlm = 100 \)). 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 3D config space.

If we look at the \( n=2 \) excited states, we get perturbation theory estimates for the energies of the \( 2^4S, 2^4P, 2^3S \) and \( 2^3P \) states:

\[
\begin{align*}
\text{J}_{20} & \quad \frac{1}{2} \left( 2^4S \right) \\
2^3S & \quad 2K_{20} \\
\text{J}_{21} & \quad \frac{1}{2} \left( 2^3P \right) \\
2^3P & \quad 2K_{21}
\end{align*}
\]

The direct integrals \( J_{2l} \) are an increasing fn. of \( l \), which lies behind the staircase effect; the physics of this is the fact
that larger I means the wave func. for the outer electron is at a larger radius, hence more effectively screened by inner electron. This is the same explanation as in the alkalies.

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 $V_{12}$ 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 func (config $1s^2$) of $H_0$ used above:

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

It is just the product of 2 H-like ground state wave funs. 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
reduced effective nuclear charge, call it $Z_e = Z_{\text{effective}}$. 

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

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

It is the product of two H-like grid states, with an effec. nuclear charge. We regard $Z_e$ as a variational parameter; we find the best choice of $Z_e$ by minimizing $\langle \Psi_{\text{trial}} | H | \Psi_{\text{trial}} \rangle$ w.r.t. $Z_e$.

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

The expectation value we need is

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

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 w.r.t. its own ground state. The result is just $-\frac{Z_e^2}{2}$, the ground state energy.
The 2nd term gives the same answer (just mult by 2).

As for the term \((Ze - Z)(\frac{1}{\ell_1} + \frac{1}{\ell_2})\), these it gives \(2 \times (Ze - Z)\) times the single particle exper. val. of \(\frac{1}{\ell}\), which is Ze (see Eq. (1.25)). So this term gives

\[2 (Ze - Z) Ze.\]

The last term \(\frac{1}{\ell_{12}}\) gives an exper. val. that can be evaluated just like we did in the path treatment of the ground state (see notes for 1/24/00, p.5) but with Ze instead of Z. The answer is \(5/8 Ze\). Altogether,

\[F(Ze) = \langle \psi | H | \psi \rangle = 2 \left( - \frac{Ze^2}{2} \right) + 2 (Ze - Z) Ze + \frac{5}{8} Ze\]

\[= Ze^2 - 2Ze^2 + \frac{5}{8} Ze.\]

The wave func. \(\psi\) is normalized for all values of Ze, so we don't need any Lagrange multipliers to enforce normalization.

To minimize \(F(Ze)\), just use calculus:

\[\frac{\partial F}{\partial Ze} = 2Ze - 2Ze + \frac{5}{8} = 0 \Rightarrow Ze = Z - 5/16\]

We see that each electron screens 5/16 of a nuclear charge from the other electron. When we evaluate \(F(Ze)\) at this
value of $Z_e$, we get the variational estimate of the ground state energy:

$$F(Z - \frac{5}{16}) = -Z^2 + \frac{5}{8}Z - \frac{25}{256}.$$ 

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

Here is a table of actual numbers:

<table>
<thead>
<tr>
<th>Atom</th>
<th>$Z$</th>
<th>$Z_{eff}$</th>
<th>$E_{\text{var}}^{(0)}$</th>
<th>$E_{\text{var}}^{(1)}$</th>
<th>$E_{\text{var}}^{(2)}$</th>
<th>$E_{\text{exact}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^-$</td>
<td>1</td>
<td>$\frac{1}{16}$</td>
<td>-1</td>
<td>-0.375</td>
<td>-0.473</td>
<td>-0.528</td>
</tr>
<tr>
<td>He</td>
<td>2</td>
<td>$\frac{1}{16}$</td>
<td>-4</td>
<td>-2.75</td>
<td>-2.848</td>
<td>-2.904</td>
</tr>
</tbody>
</table>

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