6 Atomic Structure

6.1 Variational principle

It’s a useful trick to compute ground state energy and wave function of a system which is hard to solve exactly, by making a guess! Particularly ground state energies are given quite accurately if your guess contains a little intuition...

Let $|n\rangle$, $E_n$ be complete set of e’vectors and e’values fot $H$, and choose any “trial state” $|\phi\rangle$ which is a guess for the ground state. Completeness $\implies$

$$|\phi\rangle = \sum_n c_n |n\rangle$$

and now construct

$$\frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2}$$

$$\geq \frac{\sum_n |c_n|^2 E_0}{\sum_n |c_n|^2} = E_0$$

since $E_0$ is smaller than all other $E_n$ by definition and $|c_n|^2 \geq 0$. Thus

$$\star \quad \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \text{ is a rigorous upper bound to the}$$

$$\text{ground state energy for any } |\phi\rangle$$

Game is then to choose for $|\phi\rangle$ a form which is reasonable and contains a parameter (or more than one) which may be varied to minimize this upper bound.

Example: ground state of 3D SHO. We know exact answer, $\psi \propto e^{-r^2/2x_0^2}$ where $x_0 = (\hbar/m\omega)^{1/2}$. Suppose we didn’t, might guess solution was spherically symmetric and decayed exponentially for large distances. So we’d choose trial wave function

$$|\phi\rangle = e^{-\alpha r}$$
Now we need to calculate $\langle \phi | \phi \rangle$ and $\langle \phi | H | \phi \rangle$, where $H = \hat{p}^2/2m + m\omega^2 r^2/2$. First
\[
\langle \phi | \phi \rangle = \int d^3r |\phi(r)|^2 = 4\pi \int_0^\infty r^2 dr \ e^{-2\alpha r} = \frac{4\pi}{8\alpha^3} \int_0^\infty \frac{x^2}{2} e^{-x} = \frac{\pi}{\alpha^3}.
\] (6)

For the next calculation we will need result $\nabla \phi(r) = -\alpha \frac{r}{r} e^{-\alpha r}$, giving
\[
\langle \phi | \nabla^2 | \phi \rangle = -\langle \nabla \phi | \nabla \phi \rangle = \alpha^2 \cdot 4\pi \int r^2 dr \ e^{-2\alpha r} = -\frac{\pi}{\alpha}.
\] (7)

so
\[
\langle \phi | \hat{p}^2/2m | \phi \rangle = \frac{\pi \hbar^2}{2m \alpha}
\] (8)

and finally,
\[
\langle \phi | r^2 | \phi \rangle = 4\pi \int_0^\infty r^2 dr \ r^2 e^{-2\alpha r} = \frac{3\pi}{\alpha^5}
\] (9)

So variational ground state energy for fixed $\alpha$ is
\[
E(\alpha) = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{3\pi \omega^2}{2\alpha^5} + \frac{\pi \hbar^2}{2m \alpha} = \frac{\hbar^2}{2m \alpha^2} + \frac{3m\omega^2}{2 \alpha^2}
\] (10)

Extremum given by
\[
\frac{\partial E}{\partial \alpha^2} = 0 = \frac{\hbar^2}{2m} - \frac{3m\omega^2}{2 \alpha^4}
\]

\[\Rightarrow \alpha = \left(\frac{3m^2\omega^2}{\hbar^2}\right)^{1/4} = 3^{1/4}/x_0 \tag{11}\]

so

\[
E(\alpha_{\text{min}}) = \sqrt{3}\hbar\omega \simeq 1.732\hbar\omega \tag{12}
\]

to be compared to exact answer of \(E_0 = (3/2)\hbar\omega\). Not bad, particularly when you think that the wave fctn we chose, \(e^{-3^{1/4}r/x_0}\), is exponentially large compared to the true wave fctn, \(e^{-r^2/2x_0^2}\) at large distances. This is because for short distances \(r\), where the expectation value is peaked, the contributions to the energy are of order \(\epsilon^2\) if error in wave function is \(\epsilon\).

### 6.2 Helium ground state

Helium has atomic number (\# protons) \(Z = 2\), therefore 2 electrons, and 2 neutrons to boot. Assuming nucleus is nailed down at center of coordinate system, Hamiltonian is

\[
H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \tag{13}
\]

where \(r_1\) and \(r_2\) are the distances of the 2 electrons from the nucleus, and \(r_{12}\) is the distance between electrons. Take trial wave fctn.

\[
\phi = e^{-\alpha(r_1+r_2)} \tag{14}
\]

i.e. ind. of angles, so certainly an \(\ell = 0\) state, which we expect exact ground state to be. From SHO problem in last section already know normalizing factor

\[
\langle \phi|\phi \rangle = \int d^3r_1 e^{-2\alpha r_1} \cdot \int d^3r_2 e^{-2\alpha r_2} = \frac{\pi^2}{\alpha^6} \tag{15}\]
\[ \langle \phi | \frac{\hat{p}_1^2}{2m} | \phi \rangle = \langle \phi | \frac{\hat{p}_2^2}{2m} | \phi \rangle = \frac{\pi}{\alpha^3} \cdot \frac{\pi \hbar^2}{2m \alpha} \quad (16) \]
\[ \langle \phi | \frac{1}{r_1} | \phi \rangle = \langle \phi | \frac{1}{r_2} | \phi \rangle = \frac{\pi}{\alpha^3} \cdot 4\pi \int r^2 dr \frac{e^{-2\alpha r}}{r} \quad (17) \]
\[ = \frac{\pi^2}{\alpha^5} \quad (18) \]

and
\[ \langle \phi | \frac{1}{r_{12}} | \phi \rangle = \int d^3r_1 d^3r_2 \frac{e^{-2\alpha (r_1+r_2)}}{r_{12}} \quad (19) \]
\[ = \frac{1}{32\alpha^5} \int d^3x_1 d^3x_2 \frac{e^{-x_1-x_2}}{x_{12}} \quad (20) \]

where \( r = \frac{x}{2\alpha} \). Integrals look messy, six variables all coupled because of \( x_{12} = |\mathbf{x}_1 - \mathbf{x}_2| \). Use cute trick: note that \( \int d^3x_2 \ e^{-x_2}/x_{12} \) is potential of charge distribution \( \rho(x_2) = e^{-x_2} \), evaluated at point at radius \( x_1 \). Electric field is \( E(x_1) = \int_0^{x_1} d^3x_2 \ e^{-x_2}/x_1 \) by Gauss’s law. Potential is

\[ V(x_1) = -\int_{\infty}^{x_1} \frac{dx'}{x'^2} \int_0^{x'} d^3x_2 \ e^{-x_2} \quad (21) \]
\[ = \int_{x_1}^{\infty} \frac{dx'}{x'^2} \int_0^{x_1} d^3x_2 \ e^{-x_2} + \int_{x_1}^{\infty} \frac{dx'}{x'^2} \int_{x_1}^{x'} d^3x_2 \ e^{-x_2} \quad (22) \]
\[ = \frac{4\pi}{x_1} \left[ 2 - e^{-x_1} (2 + x_1) \right] \quad (23) \]

So
\[ \langle \phi | \frac{1}{r_{12}} | \phi \rangle = \frac{16\pi^2}{32\alpha^5} \int_0^{\infty} dx_1 \ x_1 \ e^{-x} \left[ 2 - e^{-x_1} (2 + x_1) \right] \quad (24) \]
\[ = \frac{\pi^2}{2\alpha^5} \left( \frac{5}{4} \right) = \frac{5\pi^2}{8\alpha^5} \quad (25) \]

So variational energy
\[ E_{0}^{\text{var}} = \frac{\alpha^6}{\pi^2} \left( \frac{\pi^2 \hbar^2}{m \alpha^4} - \frac{4\pi^2 e^2}{\alpha^5} + \frac{5\pi^2 e^2}{8\alpha^5} \right) \tag{26} \]

\[ = \frac{\hbar^2 \alpha^2}{m} - \frac{27}{8} e^2 \alpha \tag{27} \]

Minimize:

\[ \frac{dE_{0}^{\text{var}}}{d\alpha} = 0 = \frac{2\hbar^2 \alpha}{m} - \frac{27}{8} e^2, \quad \alpha = \frac{27 e^2 m}{16 \hbar^2} \tag{28} \]

so at minimum variational energy is

\[ E_{0}^{\text{var}}(\alpha_{\text{min}}) = - \left( \frac{27}{16} \right)^2 \frac{m e^4}{\hbar^2}. \tag{29} \]

Recall 1 Ryd = \((me^4)/(2\hbar^2)\), so estimate is \(- (27/16)^2 \cdot 2 \cdot 1 \text{ Ryd} \simeq -77.5 \text{ eV} \). Measured value is \(-79.0 \text{ eV} \)-lower, of course.

6.3 He excited states

How can we use var. princ. to say anything about excited states? Theorem explicitly says \( E_{0}^{\text{var}} \geq E_0 \), ground state energy. Point is if \([\hat{O}, H] = 0\) for some operator \(\hat{O}\), can choose eigenstates of \(H\) to be simul. e’states of \(\hat{O}\), so IF we choose trial state \(|\phi\rangle\) to be e’state of \(\hat{O}\) as well, proof of var. princ. can be run through again, this time note that sum over all e’states \(|n\rangle\) of \(H\) will run only over those \(n\) which have same \(\hat{O}\) e’value! (i.e., other \(c_n\)’s are 0). So theorem will read

\[ \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} \geq \text{lowest energy corresponding to state with same value \(O\) as \(|\phi\rangle\)} \tag{30} \]

For atomic problems, know angular momentum always good q.-no. in absence of ext. fields, so we can take \(|\phi\rangle\) to have, e.g. \(\ell = 1\), and find following special case of theorem:

\[ \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} \geq \text{lowest energy corresponding to state with } \ell = 1 \tag{31} \]
So let’s pick trial state, but do it intelligently. First note that Hamiltonian has a new symmetry arising since there are 2 sets of coordinates, \( r_i, S_i, p_i \ldots i = 1, 2 \) for 2 electrons. Note Hamiltonian invariant under exchange operator \( P_{12} \) defined such that \( P_{12} \psi(1, 2) = \psi(2, 1) \), where \( (1, 2) \) short for \( (r_1, S_1, \ldots r_2, S_2, \ldots) \). In other words, we have \([P_{12}, H] = 0\) so can classify eigenstates as even or odd under exchange (in complete analogy with our discussion\(^1\) of parity \( \Pi \)).

Full exchange operator \( P_{12} \) exchanges all labels, but since current \( H \) doesn’t depend on spin, also invariant under the more limited symmetry \( P_{r_1 r_2} \) where we exchange only spatial coordinates. Pauli principle (see below) says can only consider 2-particle states overall \( \text{antisymmetric} \) under \( P_{12} \), \( P_{12} \psi(1, 2) = \psi(2, 1) = -\psi(1, 2) \). However can always consider functions both symmetric and antisymmetric under \( P_{r_1 r_2} \), which also commutes with \( H \).

In absence of Coulomb interaction \( e^2/r_{12} \) we would have two decoupled Hydrogen problems, so the \( \ell = 1 \) states would consist of one \( e^- \) in a hydrogenic \( \ell = 0 \) and one in \( \ell = 1 \). Since we want low-energy states, pick a \( 1s \) state \( \phi_{1s} \sim e^{-\alpha r} \) and a \( 2p \) state,\(^2\) \( \phi_{2p} \sim z e^{-\beta r} \). Let’s use this as guide to construct trial spatial\(^3\) wave fctns., but make them eigenfctns of \( P_{r_1 r_2} \):

\[
\phi_{\pm}(r_1, r_2) = \phi_{1s}(r_1)\phi_{2p}(r_2) \pm \phi_{1s}(r_2)\phi_{2p}(r_1)
\]

\[= z_2 e^{-(\alpha r_1 + \beta r_2)} \pm z_1 e^{-(\alpha r_1 + \beta r_2)} \]

Note the two functions \( \phi_{\pm} \) are even and odd respectively under exchange of spatial coordinates. Note both\(^4\) have total \( \ell = 1 \).

Have to compute same types of integrals as for ground state, except now

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\(^1\)Note crucial point is that eigenvalues of both \( P_{12} \) and \( \Pi \) must be \( \pm 1 \) since \( P_{12}^2 = 1 \) and \( \Pi^2 = 1 \).

\(^2\)Note the choice of the \( |10\rangle \) state \( \propto z \) is for convenience: by rotational symmetry could have taken any of the other two \( 2p \) states with \( \phi_{2p} \sim (x \pm iy)e^{-\alpha r} \) also-we’re only interested in the energy right now. For counting purposes note it looks as though there will be \( 2 \times 3 = 6 \) spatial states, but Pauli principle will not allow any of them to be multiplied by any spin wave fctn. See below.

\(^3\)I’ll ignore the spin part of the wave fctns. for now since the energy doesn’t depend on them, but remember we can’t consider just any spin wave fctn, \( \chi_{m_s, m'_s} \), because of Pauli.

\(^4\)You are adding two angular momenta \( \ell = 0 \) and \( \ell = 1 \) here. According to the a.m. addition rules, \( |\ell_1 - \ell_2| \leq \ell \leq \ell_1 + \ell_2 \) So since one of our single-particle wave functions has \( \ell = 0 \) the sum has definite \( \ell = 1 \). More complicated for higher \( \ell \)s.
some of them have angular parts. Only quote results$^5$:

\[
E_{\ell=1,+}^{\text{var}} = -4.245 \text{Ryd} \quad ; \quad E_{\ell=1,+} = -4.247 \text{Ryd} \quad (34)
\]

\[
E_{\ell=1,-}^{\text{var}} = -4.261 \text{Ryd} \quad ; \quad E_{\ell=1,-} = -4.265 \text{Ryd} \quad (35)
\]

Questions:

1. Q: Why are variational energies more accurate than for ground state?
   A: Since 2 electrons are in relative $\ell = 1$ state, the probability of finding them near each other is smaller than in ground state, thereby reducing Coulomb energy $\langle \phi | e^2 / r_{12} | \phi \rangle$, which is what keeps our trial wave fctn. from being exact!

2. Q: Why is $E_{\ell=1,+}$ higher than $E_{\ell=1,-}$ in (34-35)? A: Electrons in spatially antisymmetric wave fctn $\phi_-$ spend less time near one another ($\phi_-(r_1 = r_2) = 0$!)

$\ell = 0$ excited states

There are also $\ell = 0$ excited states, variational wave fctns. for which one can construct by combining $\phi_{1s}$ and $\phi_{2s}$. Again we can construct even and odd eigenstates of $P_{r_1r_2}$:

\[
\phi_{\ell=0,\pm} = \phi_{1s}(r_1) \phi_{2s}(r_2) \pm \phi_{1s}(r_2) \phi_{2s}(r_1)
\]

(36)

The odd combination $\phi_{\ell=0,-}$ is about 1eV lower in energy than $\phi_{\ell=1,-}$ (why?), and the even one $\phi_{\ell=0,+} \sim$ degenerate with it.

6.4 Pauli principle revisited

So far we have neglected spin. Pauli princ. states that of all the states with spin and spatial degrees of freedom one could construct, only those which are eigenstates of $P_{12}$ with eigenvalue -1, i.e. completely antisymmetric,$^6$ occur in nature. The ground state of $He$ was spatially symmetric,

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$^5$Note for odd spatial state $\phi_-$ there will be three levels ($\ell = 1, S = 1$) which are split by spin-orbit coupling in the real He atom—see Figure. This splitting is however small, so exact result quoted in (35) is accurate reflection of error in calculation of $E_{\ell=1,-}^{\text{var}}$.

$^6$More generally, a many-fermion wave fctn. must satisfy $P_{ij} \psi(1,2,3...) = -\psi(1,2,3...) \text{ for any } i,j$. 
\( P_{r_1 r_2} \psi_0(r_1, r_2) = \psi(r_1, r_2) \). So the spin state must be antisymmetric, i.e. it must be spin singlet, \( \chi_s = (\uparrow\downarrow - \downarrow\uparrow) / \sqrt{2} \). Excited \( \ell = 1 \) states we’ve just looked at are only a bit more complicated. Note \( \phi_+ \) from (33) must go along with a spin singlet wave fctn. as well, but the spatially antisymmetric fctn. \( \phi_- \) must be multiplied by a spin triplet wave fctn. to satisfy Dr. Pauli:

\[
\begin{align*}
\psi_{\ell=1,S=0} &= \phi_+ \chi_s \quad (3 \times 1 = 3 \text{ states}) \\
\psi_{\ell=1,S=1} &= \phi_- \chi_t \quad (3 \times 3 = 9 \text{ states})
\end{align*}
\]

These sets of states are given special notations in atomic physics, e.g., since we are combining \( 1s \) and \( 2p \) electrons, a state might be referred to as \( 1s2p \). This would be suff. to specify the energy in the absence of the electron-electron interaction. Or you might find the states (37) and (38) referred to as \( ^1P \) and \( ^3P \) multiplets\(^7\), following the general form \( 2S+1L \). Upon application of the spin-orbit interaction, \( S_z \) and \( L_z \) are no longer good quantum numbers, so we use total angular momentum \( j, m_j \) to label states. The rules of combining a.m.\(^8\) show that the \( ^1P \) orbital does not split: only allowed \( j \) is \( j = 1 \) since \( S = 0 \), so in this scheme the states are called \( ^3P_1 \). The \( ^3P \) multiplet does split however, into \( ^3P_0, ^3P_1 \), and \( ^3P_2 \), where the term notation is \( 2S+1L_j \). The splittings starting from the hydrogenic levels are shown in the figure. Note the order of the fine structure splittings is reversed from that of hydrogen.\(^9\)

Make sure you can account for 12 states in every column of the Figure!

More jargon: \( S = 1 \) states of helium referred to as ortho-, \( S = 0 \) as para-helium.

We can now summarize what we have learned about the low-lying states of the \( He \) atom so far, plus I’ll add some states we haven’t considered:

\(^7\)Generalization of singlet and triplet
\(^8\)Recall allowed values of \( j \) are \( |\ell - S| \ldots \ell + S \).
Figure 1: Splitting of $He$ excited states derived from $1s2p$ hydrogenic states. First splitting due to $e^- - e^-$ interaction, second to spin-orbit coupling.

**Lifetimes**

Won’t try to calculate decay rates for any of the transitions between low-lying states in $He$, but note that in figure above the $1s2p \, ^1S$ excited state is metastable (very long lifetime!) i.e. transition a won’t occur as normal dipole transition since it involves $\Delta \ell = 0$. Transition b from the $1s2p$ para state is ok (goes fast), but the transition c from the $1s2p$ ortho state is ”forbidden” since it involves a $\Delta S = 0$, i.e. a transition due to the Zeeman coupling of the magnetic field, much smaller. The transitions e and f take place quickly (electric-dipole allowed), but the electrons then get stuck in metastable states.
Figure 2: Low-lying $He$ levels and transitions.