08 - Two-Electron Atoms

- Aim of Section:
  - Analyze electron configurations of atom/ions that consist of two electrons orbiting atomic nucleus. Applications include Helium atom.

Identical Particles - I

- Consider a system consisting of two identical particles.
- Instantaneous spatial state of system is specified by spatial wavefunction $\psi(\mathbf{x}_1, \mathbf{x}_2, t)$. Here, $\mathbf{x}_1$ and $\mathbf{x}_2$ are position vectors of two particles.
- Wavefunction tells us that probability of finding first particle between $\mathbf{x}_1$ and $\mathbf{x}_1 + d^3\mathbf{x}_1$, and second between $\mathbf{x}_2$ and $\mathbf{x}_2 + d^3\mathbf{x}_2$, at time t, is $|\psi(\mathbf{x}_1, \mathbf{x}_2, t)|^2\, d^3\mathbf{x}_1\, d^3\mathbf{x}_2$.
- However, because particles are identical, this probability must be same as probability of finding first particle between $\mathbf{x}_2$ and $\mathbf{x}_2 + d^3\mathbf{x}_2$, and second between $\mathbf{x}_1$ and $\mathbf{x_1} + \mathbf{d^3 x_1}$, at time t. (Because, in both cases, result of measurement is exactly same).

Identical Particles - II

- Hence, we conclude that

  $$|\psi(\mathbf{x}_1, \mathbf{x}_2, t)|^2 = |\psi(\mathbf{x}_2, \mathbf{x}_1, t)|^2,$$

  or

  $$\psi(\mathbf{x}_1, \mathbf{x}_2, t) = \mathrm{e}^{\,\mathrm{i}\,\varphi}\,\psi(\mathbf{x}_2, \mathbf{x}_1, t),$$

  where φ is a real constant.
- However, if we swap labels on particles 1 and 2 (which are, after all, arbitrary for identical particles), and repeat argument, we also conclude that

  $$\psi(\mathbf{x}_2, \mathbf{x}_1, t) = \mathrm{e}^{\,\mathrm{i}\,\varphi}\,\psi(\mathbf{x}_1, \mathbf{x}_2, t).$$
- Hence,

  $$\mathrm{e}^{\,2\,\mathrm{i}\,\varphi} = 1.$$
- Only solutions to previous equation are $\varphi = 0$ and $\varphi = \pi$.

Identical Particles - III

- Thus, we infer that, for a system consisting of two identical particles, wavefunction must be either symmetric or anti-symmetric under interchange of particle labels.
- That is, either

  $$\psi(\mathbf{x}_2, \mathbf{x}_1, t) = +\psi(\mathbf{x}_1, \mathbf{x}_2, t),$$

  or

  $$\psi(\mathbf{x}_2, \mathbf{x}_1, t) = -\psi(\mathbf{x}_1, \mathbf{x}_2, t).$$

- Previous argument can easily be extended to systems containing more than two identical particles.
- Conclude that wavefunction of system consisting of many identical particles must be either symmetric or anti-symmetric with respect to interchange of any two particle labels.

Identical Particles - IV

- Question of whether wavefunction of a system containing many identical particles is symmetric or anti-symmetric under interchange of labels of any two particles is determined by nature of particles themselves.
- Systems of identical particles that possess integer spin have wavefunctions that are symmetric under label interchange, and are called bosons. For instance, photons are bosons.
- Systems of identical particles that possess half-integer spin have wavefunctions that are anti-symmetric under label interchange, are are called fermions. For instance, electrons, protons, and neutrons are fermions.
- Proof of so-called spin statistics theorem (that integer/ half-integer spin particles have symmetric/anti-symmetric wavefunctions under label interchange) is very complicated, and requires relativistic quantum field theory.

Two-Electron States - I

- Consider atom/ion consisting of two electrons orbiting an atomic nucleus (e.g., He, Li^{+}, Be^{++}).
- Electrons are spin-$1/2$ particles, and are, therefore, fermions.
- Let $|1,2\rangle$ be energy eigenstate of system, where 1, 2 are electron labels.
- A simple generalization of previous arguments tells us that we require

$$|2,1\rangle = -|1,2\rangle. \tag{1}$$

- However,

$$|1,2\rangle = \psi(\mathbf{x}_1,\mathbf{x}_2)\,\chi(1,2),$$

  where $\psi(\mathbf{x}_1,\mathbf{x}_2)$ is a two-particle spatial wavefunction (which tells us probable locations of two electrons in space), and $\chi(1,2)$ is a two-particle spinor (which tells us probable spin states of electrons).

Two-Electron States - II

- (1) implies that either

$$\psi(\mathbf{x}_2, \mathbf{x}_1) = +\psi(\mathbf{x}_1, \mathbf{x}_2),$$
$$\chi(2, 1) = -\chi(1, 2),$$

  or

$$\psi(\mathbf{x}_2, \mathbf{x}_1) = -\psi(\mathbf{x}_1, \mathbf{x}_2),$$
$$\chi(2, 1) = +\chi(1, 2),$$

- In other words, in order to ensure that total quantum state is anti-symmetric under label interchange, either spatial wavefunction is symmetric and spinor is anti-symmetric, or vice versa.

Two-Electron States - III

- When spin-$1/2$ is added to spin-$1/2$, result is either spin-0 or spin-1.
- There is one spin-0 state, known as singlet state.
- Singlet spinor takes form

$$\chi_{\rm singlet}(1,2) = \frac{1}{\sqrt{2}}\,(\chi_+^{(1)}\,\chi_-^{(2)} - \chi_-^{(1)}\,\chi_+^{(2)}).$$

- Here, arguments of spinor are electron labels.
- Moreover, $\chi_+^{(1)}$ represents electron 1 in spin-up state, et cetera.
- Note that, in singlet state, if measurement of S_z of one electron yields result $\pm\hbar/2$ then simultaneous measurement of S_z for other electron necessarily yields result $\mp\hbar/2$.

Two-Electron States - IV

- There are three spin-1 states, known as triplet states.
- Triplet spinor takes form

$$\begin{aligned}
\chi_{\rm triplet}(1,2;1) &= \chi_+^{(1)}\,\chi_+^{(2)},\\
\chi_{\rm triplet}(1,2;0) &= \frac{1}{\sqrt{2}}\,(\chi_+^{(1)}\,\chi_-^{(2)} + \chi_-^{(1)}\,\chi_+^{(2)}),\\
\chi_{\rm triplet}(1,2;-1) &= \chi_-^{(1)}\,\chi_-^{(2)}.
\end{aligned}$$

- Here first two arguments of spinor are electron labels.
- Third argument is conventional quantum number measuring projection of total spin along z-axis.

Two-Electron States - V

- Note that

$$\chi_{\rm singlet}(2,1) = -\chi_{\rm singlet}(1,2),$$
$$\chi_{\rm triplet}(2,1;m_S) = +\chi_{\rm triplet}(1,2;m_S),$$

  where $m_S = 0, \pm 1$.
- Thus, singlet spinor is anti-symmetric with respect to interchange of electron labels. So, corresponding spatial wavefunction must be symmetric.
- Likewise, triplet spinor is symmetric with respect to interchange of electron labels. So, corresponding spatial wavefunction must be anti-symmetric.

Two-Electron States - VI

- Symmetry requirements imply that spin-0 quantum state takes form

$$|1,2\rangle_{\rm singlet} = \psi_a(\mathbf{x}_1)\,\psi_a(\mathbf{x}_2)\,\chi_{\rm singlet}(1,2), \tag{2}$$

or

$$|1,2\rangle_{\rm singlet} = \frac{1}{\sqrt{2}}\left[\psi_a(\mathbf{x}_1)\,\psi_b(\mathbf{x}_2) + \psi_b(\mathbf{x}_1)\,\psi_a(\mathbf{x}_2)\right]\chi_{\rm singlet}(1,2). \tag{3}$$

- Here, $\psi_a(\mathbf{x})$ and $\psi_b(\mathbf{x})$ are properly normalized, mutually orthogonal, distinguishable, single-electron spatial wavefunctions.
- So, spin-0 state is combination of symmetric spatial wavefunction and anti-symmetric spinor.

Two-Electron States - VII

- Symmetry requirements imply that spin-1 quantum state takes form

$$|1,2;m_S\rangle_{\rm triplet} = \frac{1}{\sqrt{2}}\left[\psi_a(\mathbf{x}_1)\,\psi_b(\mathbf{x}_2) - \psi_b(\mathbf{x}_1)\,\psi_a(\mathbf{x}_2)\right]\chi_{\rm triplet}(1,2;m_S). \tag{4}$$

- So, spin-1 state is combination of anti-symmetric spatial wavefunction and symmetric spinor.
- Note that, unlike a spin-0 state, electrons cannot have same spatial wavefunction in spin-1 state. (Otherwise, $|1,2;m_S\rangle_{\rm triplet} = 0$, which corresponds to absence of quantum state.)
- This is manifestation of Pauli exclusion principle, which states that requirement that overall wavefunction be anti-symmetric with respect to label interchange makes it impossible for two electrons to occupy single-particle quantum states characterized by same set of quantum numbers.

Two-Electron States - VIII

- Mean-square distance between two electrons is

$$\langle|\mathbf{x}_1-\mathbf{x}_2|^2\rangle=\langle|\mathbf{x}_1|^2+|\mathbf{x}_2|^2-2\,\mathbf{x}_1\cdot\mathbf{x}_2\rangle.$$

- For singlet state (2), in which electrons are in same spatial quantum state, we get

$$\begin{aligned}\langle|\mathbf{x}_1-\mathbf{x}_2|^2\rangle&=\langle\psi_a(\mathbf{x}_1)\,\psi_a(\mathbf{x}_2)||\mathbf{x}_1|^2+|\mathbf{x}_2|^2-2\,\mathbf{x}_1\cdot\mathbf{x}_2|\psi_a(\mathbf{x}_1)\,\psi_a(\mathbf{x}_2)\rangle\\&=2\,\langle|\mathbf{x}|^2\rangle_a-2\,\langle\mathbf{x}\rangle_a\cdot\langle\mathbf{x}\rangle_a.\end{aligned}\tag{5}$$

Two-Electron States - IX

- For singlet state (3), and triplet state (4), in which electron are in different spatial quantum states, we get

$$\langle|\mathbf{x}_1-\mathbf{x}_2|^2\rangle=\frac{1}{2}\langle[\psi_a(\mathbf{x}_1)\,\psi_b(\mathbf{x}_2)\pm\psi_b(\mathbf{x}_1)\,\psi_a(\mathbf{x}_2)]|\,|\mathbf{x}_1|^2+|\mathbf{x}_2|^2-2\,\mathbf{x}_1\cdot\mathbf{x}_2|\\ [\psi_a(\mathbf{x}_1)\,\psi_b(\mathbf{x}_2)\pm\psi_b(\mathbf{x}_1)\,\psi_a(\mathbf{x}_2)]\rangle,$$

  where upper/lower signs correspond to singlet/triplet states.

- Previous expression reduces to

$$\langle|\mathbf{x}_1-\mathbf{x}_2|^2\rangle=\langle|\mathbf{x}|^2\rangle_a+\langle|\mathbf{x}|^2\rangle_b-2\,\langle\mathbf{x}\rangle_a\cdot\langle\mathbf{x}\rangle_b\mp 2\,|\langle a|\mathbf{x}|b\rangle|^2. \tag{6}$$

- Final term on right-hand side of previous expression is due to symmetry requirements (i.e., it would be absent if there were no symmetry requirements on spatial wavefunction, which would be case if two electrons were distinguishable).

Two-Electron States - X

- Comparison of (5) and (6) reveals that when electrons are in different spatial quantum states, symmetry requirements cause electrons to be, on average, closer together (than would be case in absence of symmetry requirements) when overall spatial wavefunction is symmetric with respect to label interchange, and further apart when overall spatial wavefunction is anti-symmetric with respect to label interchange.
- Thus, electrons in singlet state are, on average, closer together than electrons in corresponding triplet state.

Two-Electron Atom - I

- Two-electron atom consists of nucleus of charge $Z\,e$ surrounded by two electrons.
- Let nucleus lie at origin of our coordinate system, and let position vectors of two electrons be $\mathbf{x}_1$ and $\mathbf{x}_2$, respectively.
- Hamiltonian of system takes form

$$H = -\frac{\hbar^2}{2\,m_e}\left(\nabla_1^2+\nabla_2^2\right) - \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{|\mathbf{x}_1-\mathbf{x}_2|}\right), \tag{7}$$

  where $r_{1,2} = |\mathbf{x}_{1,2}|$.
- We have neglected any reduced mass effects.

Two-Electron Atom - II

- Terms on right-hand side of (7) represent kinetic energy of first electron, kinetic energy of second electron, electrostatic attraction between nucleus and first electron, electrostatic attraction between nucleus and second electron, and electrostatic repulsion between two electrons, respectively.
- It is final term that causes all of difficulties.
- If this term is neglected then we can write

$$H = H_1 + H_2,$$

where

$$H_{1,2} = -\frac{\hbar^2}{2\, m_e}\, \nabla_{1,2}^2 - \frac{Z\, e^2}{4\pi\, \epsilon_0\, r_{1,2}}. \tag{8}$$

Two-Electron Atom - III

- In other words, Hamiltonian just becomes sum of separate hydrogenic Hamiltonians for each electron.
- In this case, spatial wavefunctions in (2), (3), and (4) just become hydrogenic wavefunctions calculated with nuclear charge $Z\,e$.
- Let us denote these wavefunction as the $\psi_{n,l,m}(\mathbf{x})$, where n, l, and m are standard quantum numbers for a hydrogenic wavefunction.
- We know that

$$H_{1,2}\,\psi_{n,l,m}(\mathbf{x}_{1,2}) = \frac{Z^2\,E_0}{n^2}\,\psi_{n,l,m}(\mathbf{x}_{1,2}),$$

where E_0 is hydrogen ground-state energy.

Two-Electron Atom - IV

- Singlet state (2) becomes

$$|n, l, m; n, l, m\rangle_{\rm singlet} = \psi_{n,l,m}(\mathbf{x}_1)\,\psi_{n,l,m}(\mathbf{x}_2)\,\chi_{\rm singlet}, \tag{9}$$

  and has energy

$$E_{n,l,m;n,l,m} = \frac{2\,Z^2\,E_0}{n^2}.$$

Two-Electron Atom - V

- Singlet state (3) becomes

$$|n, l, m; n', l', m'\rangle_{\rm singlet} = \frac{1}{\sqrt{2}}\left[\psi_{n,l,m}(\mathbf{x}_1)\,\psi_{n',l',m'}(\mathbf{x}_2)\right. \qquad (10)$$

$$\left. + \psi_{n',l',m'}(\mathbf{x}_1)\,\psi_{n,l,m}(\mathbf{x}_2)\right]\chi_{\rm singlet},$$

  and has energy

$$E_{n,l,m;n',l',m'} = \frac{Z^2 E_0}{n^2} + \frac{Z^2 E_0}{n'^2}.$$

- Here, it is understood that $n,\ l, m \neq n',\ m',\ l'$.

Two-Electron Atom - VI

- Triplet state (4) becomes

$$|n, l, m; n', l', m'\rangle_{\rm triplet} = \frac{1}{\sqrt{2}}\left[\psi_{n,l,m}(\mathbf{x}_1)\,\psi_{n',l',m'}(\mathbf{x}_2) - \psi_{n',l',m'}(\mathbf{x}_1)\,\psi_{n,l,m}(\mathbf{x}_2)\right]\chi_{\rm triplet}, \tag{11}$$

and has energy

$$E_{n,l,m;n',l',m'} = \frac{Z^2\,E_0}{n^{\,2}} + \frac{Z^2\,E_0}{n'^{\,2}}.$$

Two-Electron Atom - VII

- In all cases, in absence of electron repulsion, energy of two-electron state just depends on n quantum numbers of two electrons.
- Hence, we can write

$$H\,|n, n'\rangle = E_{n,n'}\,|n, n'\rangle,$$

where

$$E_{n,n'} = \frac{Z^2\,E_0}{n^{\,2}} + \frac{Z^2\,E_0}{n'^{\,2}}$$

Helium Atom - I

- Consider Helium atom, for which $Z = 2$.
- Our prediction for energy of ground-state is

$$E_{1,1} = 8\,E_0 = -108.85\,\mathrm{eV}.$$

- Our prediction for energy of singly-excited state (where one electron is in $n = 1$ state and other is in $n > 1$ state) is

$$E_{1,n} = 4\left(1 + \frac{1}{n^2}\right)E_0 = -54.4\left(1 + \frac{1}{n^2}\right)\mathrm{eV}.$$

Helium Atom - II

- Our prediction for energy of singly-ionized state, where one electron has been completely removed from atom (but has no kinetic energy), and other remains in ground-state, is

$$E_{1,\infty} = 4\,E_0 = -54.42\,\mathrm{eV}.$$

- Note that singly-excited states merge into continuum at energy of singly-ionized state.
- Our prediction for energy of doubly-ionized state, where both electrons have been completely removed from atom, is

$$E_{\infty,\infty} = 0.$$

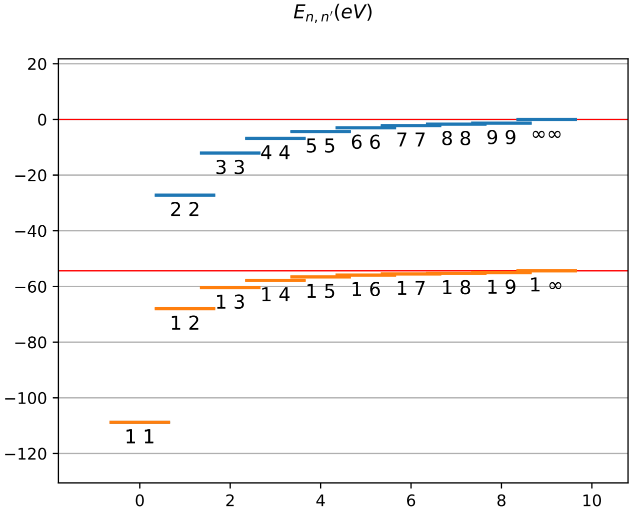
Helium Atom - III

- Our prediction for energies of doubly-excited states (in which neither electron is in $n = 1$ state) is

$$\begin{aligned} E_{n>1,n'>1} &= 4\left(\frac{1}{n^{2}} + \frac{1}{n'^{2}}\right) E_0 \\ &= 4\,E_0 - 4\left(1 - \frac{1}{n^{2}} - \frac{1}{n'^{2}}\right) E_0 \\ &= -54.42\,\mathrm{eV} + 54.42\left(1 - \frac{1}{n^{2}} - \frac{1}{n'^{2}}\right) \mathrm{eV}. \end{aligned}$$

- Final term on right-hand side of previous expression is positive, and is larger than or equal to $27.21\,\mathrm{eV}$.
- Hence, we deduce that energies of all doubly-excited states lie well above energy of singly-ionized state.

Helium Atom - IV



Helium Atom - V

- Doubly-excited states can decay to singly-ionized state (which has lower energy), a process known as auto-ionization. This process takes place comparatively rapidly.
- Follows that doubly-excited states are not really bound states, because they spontaneously ionize almost immediately after they form.
- In following, we will concentrate on true bound states of Helium atom, which consist of ground-state and singly-excited states.

Influence of Electron-Electron Repulsion Term - I

- By neglecting electron-electron repulsion term in Hamiltonian, we have derived expressions for wavefunctions and energies of Helium atom energy eigenstates.
- Our prediction for energy of ground-state is

$$E_{1,1} = -108.85\,\mathrm{eV}.$$

- However, experimentally measured ground-state energy is

$$E_{1,1} = -78.98\,\mathrm{eV}.$$

- Large discrepancy between previous two figures demonstrates that neglected electron-electron repulsion term makes large contribution to Helium atom ground-state energy.

Influence of Electron-Electron Repulsion Term - II

- We can write Hamiltonian (7) in form

  $$H = H_1 + H_2 + V_{ee},$$

  where $H_{1,2}$ are defined in (8), and

  $$V_{ee} = \frac{e^2}{4\pi\,\epsilon_0}\,\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}$$

  is electron-electron repulsion term.
- Let us treat V_{ee} as a perturbation. (This is a questionable approach because V_{ee} is not really small compared to other terms in Hamiltonian.)

Influence of Electron-Electron Repulsion Term - III

- Eigenstates of unperturbed Hamiltonian are specified in (2), (3), and (4).
- Ground-state takes form

$$|1,0,0\rangle_{\rm singlet} = \psi_{n,l,m}(\mathbf{x}_1)\,\psi_{n,l,m}(\mathbf{x}_2)\,\chi_{\rm singlet}. \tag{12}$$

- Singly-excited states take form

$$|n,l,m\rangle_{\rm singlet} = \frac{1}{\sqrt{2}}\left[\psi_{1,0,0}(\mathbf{x}_1)\,\psi_{n,l,m}(\mathbf{x}_2) + \psi_{n,l,m}(\mathbf{x}_1)\,\psi_{1,0,0}(\mathbf{x}_2)\right]\chi_{\rm singlet}, \tag{13}$$

$$|n,l,m\rangle_{\rm triplet} = \frac{1}{\sqrt{2}}\left[\psi_{1,0,0}(\mathbf{x}_1)\,\psi_{n,l,m}(\mathbf{x}_2) - \psi_{n,l,m}(\mathbf{x}_1)\,\psi_{1,0,0}(\mathbf{x}_2)\right]\chi_{\rm triplet}. \tag{14}$$

Influence of Electron-Electron Repulsion Term - IV

- Expectation value of full Hamiltonian, with respect to states (12)–(14), is

$$E_{1,0,0,\mathrm{singlet}} = 2\,Z^2\,E_0 + \langle 1,1,0|V_{ee}|1,0,0\rangle_{\mathrm{singlet}}$$

$$E_{n,l,m,\mathrm{singlet}} = \left(1+\frac{1}{n^2}\right)Z^2\,E_0 + \langle n,l,m|V_{ee}|n,l,m\rangle_{\mathrm{singlet}},$$

$$E_{n,l,m,\mathrm{triplet}} = \left(1+\frac{1}{n^2}\right)Z^2\,E_0 + \langle n,l,m|V_{ee}|n,l,m\rangle_{\mathrm{triplet}}.$$

- Here, it is understood that $n > 1$.
- Note that we are keeping Z as a free parameter. We can give it value 2 (for Helium) later on.

Influence of Electron-Electron Repulsion Term - V

- We obtain

$$
\begin{aligned}
E_{1,0,0,\mathrm{singlet}} &= 2\, Z^2\, E_0 + J_{1,0} \\
E_{n,l,m,\mathrm{singlet}} &= \left(1 + \frac{1}{n^2}\right) Z^2\, E_0 + J_{n,l} + K_{n,l}, \\
E_{n,l,m,\mathrm{triplet}} &= \left(1 + \frac{1}{n^2}\right) Z^2\, E_0 + J_{n,l} - K_{n,l}.
\end{aligned}
$$

Influence of Electron-Electron Repulsion Term - VI

- Here,

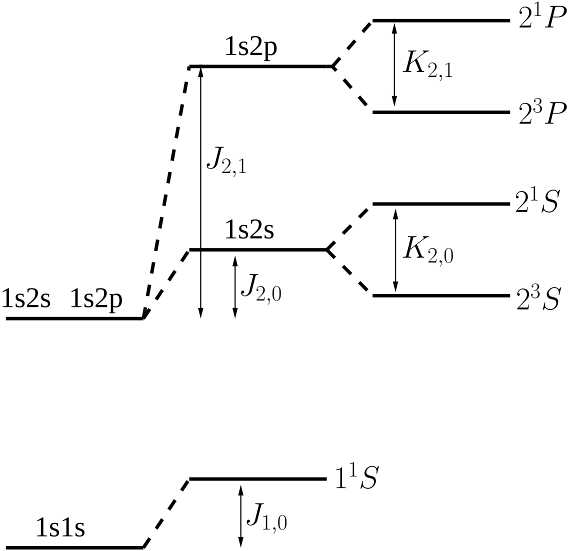
$$J_{n,l} = \iint |\psi_{1,0,0}(\mathbf{x}_1)|^2 \,\frac{e^2}{4\pi\,|\mathbf{x}_1 - \mathbf{x}_2|}\, |\psi_{n,l,m}(\mathbf{x}_2)|^2 \, d^3\mathbf{x}_1 \, d^3\mathbf{x}_2,$$

  is known as Coulomb integral, and is manifestly positive.
- Moreover,

$$K_{n,l} = \iint \psi^*_{1,0,0}(\mathbf{x}_1)\, \psi^*_{n,l,m}(\mathbf{x}_2)\, \frac{e^2}{4\pi\,|\mathbf{x}_1 - \mathbf{x}_2|}\, \psi_{1,0,0}(\mathbf{x}_2)\, \psi_{n,l,m}(\mathbf{x}_1)\, d^3\mathbf{x}_1 \, d^3\mathbf{x}_2,$$

  is known as exchange integral. It turns out that $K_{n,l}$ is also positive, but is smaller than $J_{n,l}$.
- Have suppressed m label on $J_{n,l}$ and $K_{n,l}$ because these integrals turn out to be independent of m quantum number.
- Exchange integral is consequence of symmetry requirements on wavefunction. It would be absent if electrons were distinguishable.

Influence of Electron-Electron Repulsion Term - VII



Influence of Electron-Electron Repulsion Term - VIII

- Figure on previous slide illustrates effect of electron-electron repulsion term on ground-state and $n = 2$ singly-excited states of Helium atom.
- Can label unperturbed energy eigenstates as $1s1s$, $1s2s$, and $1s2p$, which means both electrons in $1s$ (i.e., $n = 1$, $l = 0$) states, one electron in $1s$ state and other in $2s$ (i.e., $n = 2$, $l = 0$) state, and one electron in $1s$ state and other in $2p$ (i.e., $n = 2$, $l = 1$) state, respectively.
- Note that $1s2s$ and $1s2p$ states are degenerate.

Influence of Electron-Electron Repulsion Term - IX

- Can label perturbed eigenstates as $n^{2S+1}L$ states, where n is principal quantum number of excited electron, S is quantum number associated with total spin (so $2S+1=1$ for singlet state and $2S+1=3$ for triplet state), and $L=S,P,D,\cdots$ when $l=0,1,2,\cdots$. Here, l is quantum number determining overall orbital angular momentum of excited electron (which means that it also determines overall orbital angular momentum of whole atom, since other electron possess no orbital angular momentum).
- Clear from diagram that electron-electron repulsion term increases energy of 1^1S state with respect to $1s1s$ state.
- Likewise, electron-electron repulsion increases energies of $2^{1,3}S$ states with respect to $1s2s$ state.
- Electron-electron repulsion increases energies of $2^{1,3}P$ states with respect to $1s2p$ state by larger amount.
- So, electron-electron repulsion splits degeneracy of $2^{1,3}S$ and $2^{1,3}P$ states.

Influence of Electron-Electron Repulsion Term - X

- Finally, exchange integral raises energy of singlet state with respect to corresponding triplet state.
- This is not surprising. Have, seen that electrons in symmetric spatial state are, on average, closer together than electrons in corresponding anti-symmetric state. Hence, electron-electron repulsion is larger in former case.
- Singlet/triplet states have symmetric/anti-symmetric spatial wavefunctions, so electron-electron repulsion raises energy of state by larger amount in former case.

Influence of Electron-Electron Repulsion Term - XI

- Let $\mathbf{S}_1$ be spin angular momentum of first electron, let $\mathbf{S}_2$ be spin angular momentum of second electron, and let $\mathbf{S}_t = \mathbf{S}_1 + \mathbf{S}_2$.
- Follows that

$$\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle = \frac{1}{2} \langle S_t^2 - S_1^2 - S_2^2 \rangle = \frac{\hbar^2}{2} \left[S\,(S+1) - \frac{3}{2} \right],$$

  where S is conventional quantum number measuring total spin angular momentum. (So, $S = 0$ for singlet state, and $S = 1$ for triplet state.)
- Let $\boldsymbol{\sigma}_{1,2} = (\hbar/2)\,\mathbf{S}_{1,2}$.
- Follows that

$$\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \rangle = \begin{cases} -3 & \text{singlet} \\ 1 & \text{triplet} \end{cases}.$$

Influence of Electron-Electron Repulsion Term - XII

- Thus, we can write

  $$E_{n,l,m} = \left(1 + \frac{1}{n^2}\right) Z^2\, E_0 + J_{n,l} - \frac{1}{2}\left(1 + \langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \rangle\right) K_{n,l},$$

  as long as we adopt convention that $K_{1,0} = 0$.
- Previous expression implies that energy of singly-excited state of two-electron atom is spin-dependent.
- This spin depedence is electrostatic in origin, and is of magnitude $e^2/(4\pi\,\epsilon_0\,a_0)$, which means that it is of order a few electronvolts.

Influence of Electron-Electron Repulsion Term - XIII

- It is instructive to compare previous electrostatic spin dependence of energy to spin dependence arising from direct interaction of electron spins.
- Electron has magnetic moment of magnitude $\mu_e \sim e\,\hbar/m_e$.
- Magnetic moment generates magnetic field of approximate magnitude $B \sim \mu_0\,\mu_e/(4\pi\,r^3)$.
- Energy of other electron, which is situated distance $r \sim a_0$ from first, is of order $\mu_e\,B \sim \mu_0\,(e\,\hbar/m_e)^2/a_0^3$.
- Hence, we deduce that direct interaction of electron spins gives rise to contribution to energy of atom that is of order

$$\alpha^2\,\frac{e^2}{4\pi\,\epsilon_0\,a_0}\;:$$

i.e., about $10^{-4}\,\mathrm{eV}$.

Influence of Electron-Electron Repulsion Term - XIV

- Magnetic interaction of neighboring electron spins in ferromagnet is not large enough to keep spins aligned above temperature $T \sim 10^{-4}\,\mathrm{eV}/k_B \sim 5\,\mathrm{K}$ (where k_B is Boltzmann constant).
- On other hand, electrostatic interaction can keep spins aligned for temperatures below about $1\,\mathrm{eV}/k_B \sim 5 \times 10^4\,\mathrm{K}$.
- Clearly, it is electrostatic interaction of neighboring spins that is responsible for room-temperature ferromagnetism.
- Electrostatic interaction has its origin in fact that if spins are aligned/anti-aligned then spatial wavefunctions are anti-symmetric/symmetric, respectively. Former, state has lower electrostatic energy because electrons are, on average, further apart.

Calculation of Coulomb and Exchange Integrals - I

- We now need to calculate Coulomb integrals,

$$J_{n,l} = \iint |\psi_{1,0,0}(\mathbf{x}_1)|^2 \, \frac{e^2}{4\pi\,|\mathbf{x}_1 - \mathbf{x}_2|} \, |\psi_{n,l,m}(\mathbf{x}_2)|^2 \, d^3\mathbf{x}_1 \, d^3\mathbf{x}_2,$$

and exchange integrals,

$$K_{n,l} = \iint \psi^*_{1,0,0}(\mathbf{x}_1)\, \psi^*_{n,l,m}(\mathbf{x}_2) \, \frac{e^2}{4\pi\,|\mathbf{x}_1 - \mathbf{x}_2|} \, \psi_{1,0,0}(\mathbf{x}_2)\, \psi_{n,l,m}(\mathbf{x}_1) \, d^3\mathbf{x}_1 \, d^3\mathbf{x}_2.$$

Calculation of Coulomb and Exchange Integrals - II

- We know that

$$\psi_{n,l,m}(\mathbf{x}) = R_{n,l}(r)\, Y_l^m(\theta, \phi).$$

- Moreover, it can be shown that

$$\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} = \sum_{l=0,\infty} \sum_{m=-l,l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}}\, Y_l^{m\,*}(\theta_1, \phi_1)\, Y_l^m(\theta_2, \phi_2),$$

where $r_<$ is lesser of r_1 and r_2, and $r_>$ is greater.

Calculation of Coulomb and Exchange Integrals - III

- Let
$$\rho = \frac{2\,Z\,r}{a_0}.$$
- Follows that
$$R_{n,l}(r) = \left(\frac{2\,Z}{a_0}\right)^{3/2}\,\mathcal{R}_{n,l}(\rho),$$
  where
$$\mathcal{R}_{n,l}(\rho) = \left[\frac{(n-l-1)!}{2\,n^4\,(n+l)!}\right]^{1/2}\,\mathrm{e}^{-\rho/(2\,n)}\left(\frac{\rho}{n}\right)^l\,L_{n-l-1}^{2l+1}(\rho/n).$$

Calculation of Coulomb and Exchange Integrals - IV

- Obtain

$$J_{n,l} = Z\,|E_0|\,\mathcal{J}_{n,l},$$

where

$$\mathcal{J}_{n,l} = 4 \sum_{l'=0,\infty} \sum_{m'=-l',l'} \frac{1}{2l'+1}\,A_{l',m'}\,B_{l,m;l',m'}\,C_{n,l,l'},$$

$$A_{l',m'} = \oint Y_{l'}^{m'\,*}\,d\Omega,$$

$$B_{l,m;l',m'} = \oint Y_l^{m\,*}\,Y_l^m\,Y_{l'}^{m'}\,d\Omega,$$

$$C_{n,l,l'} = \int_0^\infty\!\!\int_0^\infty \rho_1^2\,\rho_2^2\,\frac{\rho_<^{l'}}{\rho_>^{l'+1}}\,[\mathcal{R}_{1,0}(\rho_1)]^2\,[\mathcal{R}_{n,l}(\rho_2)]^2\,d\rho_1\,d\rho_2.$$

Calculation of Coulomb and Exchange Integrals - IV

- Orthonormality of spherical harmonics reveals that $A_{l',m'} = \sqrt{4\pi}\,\delta_{l',0}\,\delta_{m',0}$ and $B_{l,m;0,0} = 1/\sqrt{4\pi}$.
- Hence, we get

$$\mathcal{J}_{n,l} = 4\int_0^\infty\!\!\int_0^\infty \frac{\rho_1^2\,\rho_2^2}{\rho_>}\,[\mathcal{R}_{1,0}(\rho_1)]^2\,[\mathcal{R}_{n,l}(\rho_2)]^2\,d\rho_1\,d\rho_2.$$

- However,

$$\mathcal{R}_{1,0}(\rho) = \frac{1}{\sqrt{2}}\,\mathrm{e}^{-\rho/2}.$$

- Thus, we obtain

$$\begin{aligned}\mathcal{J}_{n,l} = {} & 2\int_0^\infty \rho_2\,[\mathcal{R}_{n,l}(\rho_2)]^2\left(\int_0^{\rho_2}\rho_1^2\,\mathrm{e}^{-\rho_1}\,d\rho_1\right)d\rho_2\\ & +2\int_0^\infty \rho_2^2\,[\mathcal{R}_{n,l}(\rho_2)]^2\left(\int_{\rho_2}^\infty \rho_1\,\mathrm{e}^{-\rho_1}\,d\rho_1\right)d\rho_2.\end{aligned}$$

Calculation of Coulomb and Exchange Integrals - V

- Some straightforward integration yields final result

$$\mathcal{J}_{n,l} = 2\int_0^\infty \rho\left[2 - \mathrm{e}^{-\rho}\,(2+\rho)\right]\left[\mathcal{R}_{n,l}(\rho)\right]^2 d\rho.$$

- For case $n = 1$ and $l = 0$, we have

$$\mathcal{R}_{1,0}(\rho) = \frac{1}{\sqrt{2}}\,\mathrm{e}^{-\rho}.$$

- Hence, we obtain

$$\mathcal{J}_{1,0} = \int_0^\infty \left[2 - \mathrm{e}^{-\rho}\,(2+\rho)\right]\mathrm{e}^{-\rho}\,d\rho = \frac{5}{4}.$$

Calculation of Coulomb and Exchange Integrals - VI

- Hence, our new estimate for ground-state energy of Helium atom, which takes electron-electron repulsion into account, is

$$E_{1,0,0,\mathrm{singlet}} = 2\,Z^2\,E_0 - \frac{5\,Z}{4}\,E_0 = \frac{11}{2}\,E_0 = -74.83\,\mathrm{eV},$$

  given that $Z = 2$.

- This new estimate is much closer to experimental result (i.e., $-78.98\,\mathrm{eV}$) than our previous estimate (i.e., $-108.85\,\mathrm{eV}$) that did not take electron-electron repulsion into account.

Calculation of Coulomb and Exchange Integrals - VII

- We also obtain

$$K_{n,l} = Z\,|E_0|\,\mathcal{K}_{n,l},$$

where

$$\mathcal{K}_{n,l} = 4\sum_{l'=0,\infty}\sum_{m'=-l',l'}\frac{1}{2l'+1}\left|D_{l,m;l',m'}\right|^2 E_{n,l,l'},$$

$$D_{l,m;l',m'} = \int Y_l^{m\,*}(\theta,\phi)\,Y_{l'}^{m'}(\theta,\phi)\,d\Omega,$$

$$E_{n,l,l'} = \int_0^\infty\int_0^\infty \rho_1^2\,\rho_2^2\,\frac{\rho_<^l}{\rho_>^{l+1}}\,\mathcal{R}_{1,0}(\rho_1)\,\mathcal{R}_{n,l,l'}(\rho_1)\,\mathcal{R}_{1,0}(\rho_2)\,\mathcal{R}_{n,l}(\rho_2)\,d\rho_1\,d\rho_2$$

Calculation of Coulomb and Exchange Integrals - VIII

- Orthonormality of spherical harmonics reveals that $D_{l,m;l',m'} = \delta_{l,l'}\,\delta_{m,m'}$.
- Hence, we get

$$\mathcal{K}_{n,l} = \frac{4}{2\,l+1}\int_0^\infty\!\!\int_0^\infty \frac{\rho_1^2\,\rho_2^2\,\rho_<^l}{\rho_>^{l+1}}\,\mathcal{R}_{1,0}(\rho_1)\mathcal{R}_{n,l}(\rho_1)\mathcal{R}_{1,0}(\rho_2)\mathcal{R}_{n,l}(\rho_2)\,d\rho_1\,d\rho_2,$$

which we can write as

$$\begin{aligned}\mathcal{K}_{n,l} &= \frac{4}{2\,l+1}\int_0^\infty\!\!\int_0^{\rho_2} \frac{\rho_1^{2+l}}{\rho_2^{l-1}}\,\mathcal{R}_{1,0}(\rho_1)\mathcal{R}_{n,l}(\rho_1)\mathcal{R}_{1,0}(\rho_2)\mathcal{R}_{n,l}(\rho_2)\,d\rho_1\,d\rho_2\\ &\quad+\frac{4}{2\,l+1}\int_0^\infty\!\!\int_{\rho_2}^\infty \frac{\rho_2^{2+l}}{\rho_1^{l-1}}\,\mathcal{R}_{1,0}(\rho_1)\mathcal{R}_{n,l}(\rho_1)\mathcal{R}_{1,0}(\rho_2)\mathcal{R}_{n,l}(\rho_2)\,d\rho_1\,d\rho_2.\end{aligned}$$

Calculation of Coulomb and Exchange Integrals - IX

- If we exchange order of integration, then we deduce that

$$\int_0^\infty \int_0^{\rho_2} \frac{\rho_1^{2+l}}{\rho_2^{l-1}} \mathcal{R}_{1,0}(\rho_1)\mathcal{R}_{n,l}(\rho_1)\mathcal{R}_{1,0}(\rho_2)\mathcal{R}_{n,l}(\rho_2)\, d\rho_1\, d\rho_2$$
$$= \int_0^\infty \int_{\rho_1}^\infty \frac{\rho_1^{2+l}}{\rho_2^{l-1}} \mathcal{R}_{1,0}(\rho_1)\mathcal{R}_{n,l}(\rho_1)\mathcal{R}_{1,0}(\rho_2)\mathcal{R}_{n,l}(\rho_2)\, d\rho_2\, d\rho_1.$$

- If we now interchange variables of integration, $\rho_1 \leftrightarrow \rho_2$, then we get

$$\int_0^\infty \int_0^{\rho_2} \frac{\rho_1^{2+l}}{\rho_2^{l-1}} \mathcal{R}_{1,0}(\rho_1)\mathcal{R}_{n,l}(\rho_1)\mathcal{R}_{1,0}(\rho_2)\mathcal{R}_{n,l}(\rho_2)\, d\rho_1\, d\rho_2$$
$$= \int_0^\infty \int_{\rho_2}^\infty \frac{\rho_2^{2+l}}{\rho_1^{l-1}} \mathcal{R}_{1,0}(\rho_1)\mathcal{R}_{n,l}(\rho_1)\mathcal{R}_{1,0}(\rho_2)\mathcal{R}_{n,l}(\rho_2)\, d\rho_1\, d\rho_2.$$

Calculation of Coulomb and Exchange Integrals - X

- Hence, we deduce that

$$\mathcal{K}_{n,l} = \frac{4}{2\,l+1}\int_0^\infty \rho^{2+l}\,\mathrm{e}^{-\rho/2}\,\mathcal{R}_{n,l}(\rho)\,\mathcal{I}_{n,l}(\rho)\,d\rho,$$

  where

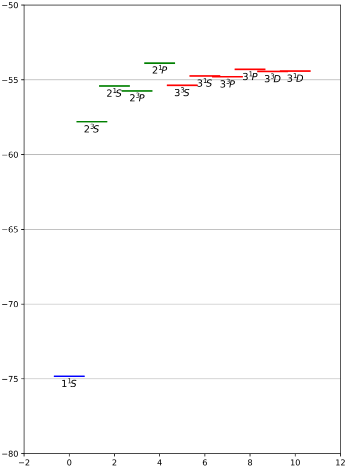
$$\mathcal{I}_{n,l}(\rho) = \int_\rho^\infty x^{1-l}\,\mathrm{e}^{-x/2}\,\mathcal{R}_{n,l}(x)\,dx.$$

- Here, we have made use of fact that $\mathcal{R}_{1,0}(\rho) = \mathrm{e}^{-\rho/2}/\sqrt{2}$.

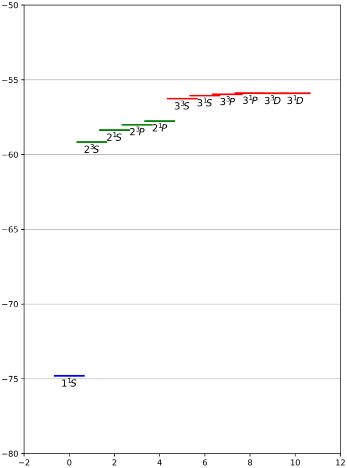
Calculation of Coulomb and Exchange Integrals - XI

- In general, the $\mathcal{J}_{n,l}$ and the $\mathcal{K}_{n,l}$, for $n > 1$, are too complicated to evaluate analytically.
- However, they are straightforward to evaluate numerically (e.g., using Python).

Calculation of Coulomb and Exchange Integrals - XII



$E_{theory}(eV)$



$E_{experiment}(eV)$

Calculation of Coulomb and Exchange Integrals - XIII

- Agreement between new theoretical calculation and experimental data is not particularly impressive.
- New theoretical calculation that includes electron-electron repulsion does get some things right.
- For instance, P states have higher energies than corresponding S states, and D states have higher energies than corresponding P states. (Recall that all these states are degenerate in absence of electron-electron repulsion).
- Also, singlet states have higher energies that corresponding triplet state.
- However, our estimates for Coulomb and exchange integrals seem to be significantly too high.
- How can we further improve calculation?

Variational Method - I

- Suppose that we wish to solve time-independent Schrödinger equation

  $$H|\psi\rangle = E|\psi\rangle,$$

  where H is known (presumably complicated) time-independent Hamiltonian.
- Let $|\psi\rangle$ be a properly normalized trial solution to previous equation.
- So-called variational principle states, quite simply, that true ground-state energy, E_0, is always less than or equal to expectation value of H calculated with trial solution: that is,

  $$E_0 \leq \langle\psi|H|\psi\rangle.$$

- Thus, by varying $|\psi\rangle$ until expectation value of H is minimized, we can obtain approximations to eigenstate and energy of ground-state.

Variational Method - II

- Let us prove variational principle.
- Suppose that the $|n\rangle$ and the E_n are true eigenstates and eigenvalues of H: that is,

$$H\,|n\rangle = E_n\,|n\rangle. \tag{15}$$

- Furthermore, let

$$E_0 < E_1 < E_2 < \cdots, \tag{16}$$

so that $|0\rangle$ is ground-state, $|1\rangle$ is first excited state, et cetera.
- The $|n\rangle$ are assumed to be orthonormal: that is,

$$\langle n|m\rangle = \delta_{nm}. \tag{17}$$

- If our trial state $|\psi\rangle$ is properly normalized then we can write

$$|\psi\rangle = \sum_n c_n\,|n\rangle,$$

where

$$\sum_n |c_n|^2 = 1. \tag{18}$$

Variational Method - III

- Expectation value of H, calculated with $|\psi\rangle$, takes form

$$\langle\psi|H|\psi\rangle = \left(\sum_n c_n^* \langle n|\right) H \left(\sum_m c_m |m\rangle\right) = \sum_{n,m} c_n^* c_m \langle n|H|m\rangle$$

$$= \sum_{n,m} c_n^* c_m \, E_m \langle n|m\rangle = \sum_n E_n |c_n|^2,$$

  where use has been made of (15) and (17).

- So, we can write

$$\langle\psi|H|\psi\rangle = |c_0|^2 E_0 + \sum_{n>0} |c_n|^2 E_n.$$

- However, (18) can be rearranged to give

$$|c_0|^2 = 1 - \sum_{n>0} |c_n|^2.$$

Variational Method - IV

- Combining previous two equations, we obtain

$$\langle\psi|H|\psi\rangle = E_0 + \sum_{n>0} |c_n|^2 \, (E_n - E_0).$$

- Second term on right-hand side of previous expression is positive definite, because $E_n - E_0 > 0$ for all $n > 0$ [see (16)].
- Hence, we obtain desired result

$$E_0 \leq \langle\psi|H|\psi\rangle.$$

Variational Method - V

- Suppose that we have found a good approximation, $|\psi_0\rangle$, to ground-state eigenstate.
- If $|\psi\rangle$ is a normalized trial state that is orthogonal to $|\psi_0\rangle$ (i.e., $\langle\psi|\psi_0\rangle = 0$) then, by repeating previous analysis, we can easily demonstrate that

$$E_1 \leq \langle\psi|H|\psi\rangle.$$

- Thus, by varying $|\psi\rangle$ until expectation value of H is minimized, we can obtain approximations to eigenstate and energy of first excited state.
- We can continue process until we have approximations to all of stationary eigenstates.
- Errors are cumulative in this method, so that approximations to highly excited states are likely to be inaccurate.
- For this reason, variational method is generally only used to calculate ground-state, and first few excited states, of complicated quantum systems.

Application to Helium Atom - I

- Our previous estimate for ground-state energy of a two-electron atom was

  $$E_{1,0,0,\text{singlet}} = 2\,Z^2\,E_0 - \frac{5\,Z}{4}\,E_0,$$

  where Z is nuclear charge.
- When evaluated for $Z = 2$ (Helium), we get

  $$E_{1,0,0,\text{singlet}} = \frac{11}{2}\,E_0 = -74.83\,\text{eV},$$

  which is 5.3% higher than experimentally measured energy.
- Can we do better?

Application to Helium Atom - II

- Suppose that we treat nuclear charge, Z, as a variable?
- If it turns out that value of Z that minimizes ground-state energy is less than true nuclear charge then we can understand reduction as consequence of partial shielding of nuclear potential seen by one electron due to negative charge of other electron.

Application to Helium Atom - III

- We can rewrite Hamiltonian of two-electron atom in form

  $$H = H_1(Z') + H_2(Z') + V_{ee} + U(Z'),$$

  where

  $$H_{1,2}(Z') = -\frac{\hbar^2}{2\,m_e}\,\nabla_{1,2}^2 - \frac{Z'\,e^2}{4\pi\,\epsilon_0\,r_{1,2}}$$

  is Hamiltonian of hydrogenic atom with nuclear charge $+Z'\,e$,

  $$V_{ee} = \frac{e^2}{4\pi\,\epsilon_0}\,\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}$$

  is electron-electron repulsion term, and

  $$U(Z') = \frac{e^2}{4\pi\,\epsilon_0}\left(\frac{Z'-Z}{r_1} + \frac{Z'-Z}{r_2}\right).$$

- Note that Z' is effective nuclear charge, while Z is true nuclear charge.

Application to Helium Atom - IV

- We shall treat $H_1(Z') + H_2(Z')$ as unperturbed Hamiltonan of system, and $V_{ee} + U(Z')$ as perturbation.
- It follows that ground-state energy is

$$E_{1,0,0,\mathrm{singlet}} = 2\,Z'^{\,2}\,E_0 + \langle V_{ee}\rangle_{1,0,0,\mathrm{singlet}} + \langle U\rangle_{1,0,0,\mathrm{singlet}}.$$

- However, we have already seen that

$$\langle V_{ee}\rangle_{1,0,0,\mathrm{singlet}} = -\frac{5\,Z'}{4}\,E_0.$$

- Moreover, it is easily demonstrated that

$$\langle U\rangle_{1,0,0,\mathrm{singlet}} = \frac{e^2}{4\pi\,\epsilon_0}\,2\,(Z'-Z)\left\langle\frac{1}{r}\right\rangle_{1,0,0,\mathrm{singlet}}.$$

Application to Helium Atom - V

- Now, we know that

$$\left\langle\frac{1}{r}\right\rangle_{1,0,0,\mathrm{singlet}} = \frac{Z'}{a_0},$$

  and $E_0 = -e^2/(8\pi\,\epsilon_0\,a_0)$, so we get

$$\langle U\rangle_{1,0,0,\mathrm{singlet}} = -4\,(Z'-Z)\,Z'\,E_0.$$

Application to Helium Atom - VI

- Hence,

$$E_{1,0,0,\text{singlet}} = 2\,Z'^{\,2}\,E_0 - \frac{5\,Z'}{4}\,E_0 - 4\,(Z' - Z)\,Z'\,E_0,$$

or

$$E_{1,0,0,\text{singlet}}(Z') = \left[-2\,Z'^{\,2} + \left(4\,Z - \frac{5}{4}\right)Z'\right]E_0, \tag{19}$$

- Ground-state energy is minimized with respect to effective nuclear charge, Z', when

$$\frac{dE_{1,0,0,\text{singlet}}}{dZ'} = \left[-4\,Z' + \left(4\,Z - \frac{5}{4}\right)Z'\right]E_0 = 0.$$

Application to Helium Atom - VII

- Thus, energy is minimized when

  $$Z' = Z - \frac{5}{16}, \tag{20}$$

  which does indicate a degree of shielding of nuclear charge seen by given electron due to presence of other electron.

- Substituting into (19), our new estimate for ground-state energy of two-electron atom becomes

  $$E_{1,0,0,\mathrm{singlet}} = 2\left(Z - \frac{5}{16}\right)^2 E_0. \tag{21}$$

- Finally, for case of Helium ($Z = 2$) we get

  $$E_{1,0,0,\mathrm{singlet}} = \frac{3^6}{2^7}\,E_0 = -77.49\,\mathrm{eV},$$

  which is 1.9% larger than experimental result.

Application to Helium Atom - VIII

- More generally, if we apply (20) and (21) to singlet ground-states of negative hydrogen ion, H^- (i.e., $Z = 1$), singly-ionized lithium ion, Li^+ (i.e., $Z = 3$), doubly-ionized beryllium ion, Be^{++} (i.e., $Z = 4$), and triply-ionized boron ion, B^{+++} (i.e., $Z = 5$), as well as neutral helium atom, He (i.e., $Z = 2$), then we get predictions tabulated below:

Z	Z'	$E_{\rm var}(\rm eV)$	$E_{\rm expt}(\rm eV)$	Error(%)
1	0.688	-12.86	-14.36	10.4
2	1.688	-77.49	-78.98	1.9
3	2.688	-196.54	-198.09	0.78
4	3.688	-370.01	-371.59	0.43
5	4.688	-597.91	-599.52	0.27

Application to Helium Atom - IX

- It can be seen that error decreases as Z increases.
- However, error for H^- ion is quite severe (10%).
- In fact, estimate for ground-state energy of H^- ($-12.86\,\mathrm{eV}$) is slightly higher than ground-state energy of neutral hydrogen atom ($-13.61\,\mathrm{eV}$).
- This prediction leads to erroneous impression that it is not energetically favorable for neutral hydrogen atom to absorb additional electron to form negative hydrogen ion. In other words, H^- ion has negative binding energy.
- Can we further improve our prediction of ground-state energy of a two-electron atom/ion?

Application to Helium Atom - X

- Let us adopt following trial ground-state:

  $$|1,0,0\rangle_{\rm singlet} = \frac{1}{\sqrt{2}}\left[\psi_1(\mathbf{x}_1)\,\psi_2(\mathbf{x}_2) + \psi_2(\mathbf{x}_1)\,\psi_1(\mathbf{x}_2)\right]\chi_{\rm singlet}, \tag{22}$$

  where

  $$\psi_1(\mathbf{x}) = \frac{1}{\sqrt{\pi}}\left(\frac{Z_1}{a_0}\right)^{3/2}\exp\left(-\frac{Z_1\,r}{a_0}\right),$$

  $$\psi_2(\mathbf{x}) = \frac{1}{\sqrt{\pi}}\left(\frac{Z_2}{a_0}\right)^{3/2}\exp\left(-\frac{Z_2\,r}{a_0}\right).$$

- ψ_1 and ψ_2 are hydrogenic ground-state wavefunctions corresponding to nuclear charges Z_1 and Z_2, respectively.

Application to Helium Atom - XI

- In effect, we are saying that each electron experiences a different nuclear charge due to shielding action of other electron.
- Calculation of expectation value of two-electron atom/ion Hamiltonian with trial ground-state (22) is straightforward, but tedious.[1]
- Result is

$$\frac{\langle H\rangle}{E_0} = \frac{x^8 - 2\,Z\,x^7 - x^6\,y^2/2 + x^5\,y^2/2 + x^3\,y^4/8 - (2\,Z - 5/8)\,x\,y^6 + y^8/2}{x^6 + y^6}, \tag{23}$$

  where $x = Z_1 + Z_2$ and $y = 2\sqrt{Z_1\,Z_2}$.
- Need to minimize (23) with respect to variations in Z_1 and Z_2.
- This can only be done numerically (e.g., using Python). Results are tabulated on next slide.

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[1] Quantum Mechanics, R. Fitzpatrick, World Scientific 2015

Application to Helium Atom - XI

Z	$Z_{\rm av}$	Z_1	Z_2	$E_{\rm var}(\rm eV)$	$E_{\rm expt}(\rm eV)$	Error(%)
1	0.661	1.039	0.283	-13.97	-14.36	2.7
2	1.686	2.183	1.189	-78.25	-78.98	0.92
3	2.687	3.295	2.079	-197.25	-198.09	0.42
4	3.687	4.388	2.985	-370.70	-371.59	0.24
5	4.687	5.473	3.901	-598.58	-599.52	0.16

- Note that $Z_{\rm av} = (Z_1 + Z_2)/2$ is almost identical to Z' from previous table. So, average nuclear charge is same as before.
- Splitting of nuclear charge is due to fact that electron-electron repulsion causes two electrons to actively avoid one another. In other words, if one electron is close to nucleus then other electron tends to be far from nucleus, and vice versa.

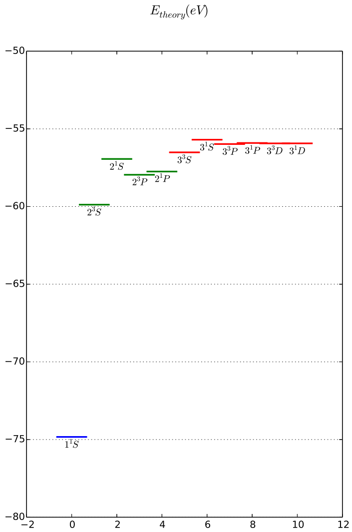
Application to Helium Atom - XII

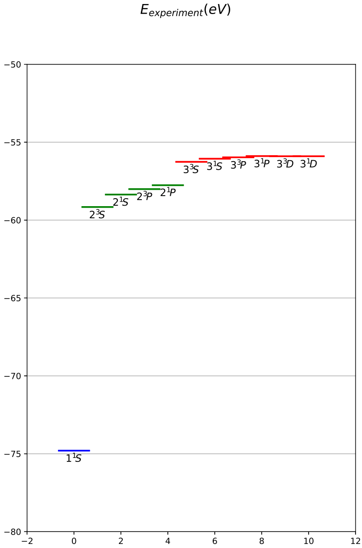
- Refined estimates for ground-state energies of two-electron atom/ion are substantially more accurate than previous estimates.
- In particular, estimate for ground-state energy of H^- ion ($-13.97\,\mathrm{eV}$) is now less than neutral hydrogen ground-state energy ($-13.61\,\mathrm{eV}$), leading to correct conclusion that H^- ion has positive binding energy.

Application to Helium Atom - XIII

- Idea of splitting of effective nuclear charge experienced by each electron in two-electron atom leads to following guess for improved calculation of Helium singly-excited states.
- Suppose that inner electron (in 1, 0, 0 state) sees full nuclear charge $2\,e$, while outer electron (in $n > 1$, l, m state) only sees charge $1\,e$ due to shielding effect of inner electron.
- Can easily perform all required integrals numerically (e.g., in Python).

Application to Helium Atom - IX





Application to Helium Atom - X

- Calculation is improvement on previous one, although splitting of 2S and $3S$ triplet and singlet states is still too large.

Spectrum of Helium - I

- Standard selection rules for radiation-induced transitions between atomic energy levels do not allow there to be a change in overall spin quantum number of atom (because, to lowest order, electromagnetic waves do not couple to electron spin).
- Hence, transitions between singlet and triplet states of Helium atom are forbidden.
- For this reason, it was originally supposed that there were two types of Helium in nature: parahelium ($S = 0$) and orthohelium ($S = 1$). (Recall that Helium was discovered via its absorption lines in spectrum of Sun.)
- Transitions between parahelium and orthohelium can actually occur, with very low probability, due to higher-order effects.

Spectrum of Helium - II

- Thus, 2^3S state (which is ground-state of orthohelium) can decay to 1^1S state (which is much lower energy ground-state of parahelium), but process takes about 8000 seconds.