Up until now, we have been ignoring spin. Let's include it.

$$\psi_{TOTAL} = \underbrace{\psi(x_1, x_2)}_{\text{spatial}} \underbrace{\chi}_{\text{spin}}$$

Refer to section 4.4.3 Addition of Spin Angular Momentum

Two spin $\frac{1}{2}$ particles, let's assume electrons for now:

| | | $\lvert s\ s_z\rangle$ |
|---|---|---|
| $s=1$ (triplet) symmetric | $\uparrow\uparrow$ | $\lvert 1\ 1\rangle$ |
| | $\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ | $\lvert 1\ 0\rangle$ |
| | $\downarrow\downarrow$ | $\lvert 1\ -1\rangle$ |
| $s=0$ (singlet) antisymmetric | $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$ | $\lvert 0\ 0\rangle$ |

---

Pauli Exclusion Principle (1925) weaker condition

In a multielectron atom there can never be more than one electron in the same quantum state

Stronger condition → A system containing several electrons must be described by an antisymmetric total eigenfunction.

What happens to $\psi_A$ when $x_1 \approx x_2$? $\psi_A \rightarrow 0$ (see picture)

In other words → $\psi_{TOTAL} = \underbrace{\psi(\vec{r}_1, \vec{r}_2)}_{\text{spatial}} \underbrace{\chi}_{\text{spin}}$ must be antisymmetric!

Fermions and Bosons

**Table 9-1** The Symmetry Character of Various Particles

| Particle | Symmetry | Generic Name | Spin ($s$) |
|---|---|---|---|
| Electron | Antisymmetric | Fermion | 1/2 |
| Positron | Antisymmetric | Fermion | 1/2 |
| Proton | Antisymmetric | Fermion | 1/2 |
| Neutron | Antisymmetric | Fermion | 1/2 |
| Muon | Antisymmetric | Fermion | 1/2 |
| $\alpha$ particle | Symmetric | Boson | 0 |
| He atom (ground state) | Symmetric | Boson | 0 |
| $\pi$ meson | Symmetric | Boson | 0 |
| Photon | Symmetric | Boson | 1 |
| Deuteron | Symmetric | Boson | 1 |

what about 3 electrons? How do you construct an antisymmetric w.f. ?

**Example 9-2.** Determine the form of the normalized antisymmetric total eigenfunction for a system of three particles, in which the interactions between the particles can be ignored.
▶This is easy to do if it is noted that the two-particle antisymmetric total eigenfunction

$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2)\right]$$

can also be written as a so-called *Slater determinant*

$$\psi_A = \frac{1}{\sqrt{2!}}\begin{vmatrix}\psi_\alpha(1) & \psi_\alpha(2)\\ \psi_\beta(1) & \psi_\beta(2)\end{vmatrix}$$

where $2! = 2 \times 1 = 2$. The identity of these two expressions can be verified by expanding the determinant. In determinantal form, the extension to three particles is obvious

$$\psi_A = \frac{1}{\sqrt{3!}}\begin{vmatrix}\psi_\alpha(1) & \psi_\alpha(2) & \psi_\alpha(3)\\ \psi_\beta(1) & \psi_\beta(2) & \psi_\beta(3)\\ \psi_\gamma(1) & \psi_\gamma(2) & \psi_\gamma(3)\end{vmatrix}$$

where $3! = 3 \times 2 \times 1 = 6$. Expansion of this determinant yields

$$\psi_A = \frac{1}{\sqrt{3!}}\left[\psi_\alpha(1)\psi_\beta(2)\psi_\gamma(3) + \psi_\beta(1)\psi_\gamma(2)\psi_\alpha(3)\right.$$
$$+ \psi_\gamma(1)\psi_\alpha(2)\psi_\beta(3) - \psi_\gamma(1)\psi_\beta(2)\psi_\alpha(3)$$
$$\left. - \psi_\beta(1)\psi_\alpha(2)\psi_\gamma(3) - \psi_\alpha(1)\psi_\gamma(2)\psi_\beta(3)\right]$$

① Electrons in the <u>triplet state</u> symmetric must have an antisymmetric spatial wave function

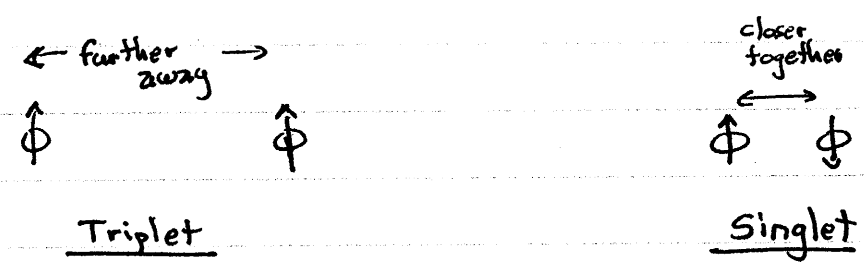
$$\psi_{TOTAL} = \psi_{\substack{anti\\symmetric}} \, \chi_{symmetric}$$

antisymmetric

② Electrons in the <u>singlet spin state</u> antisymmetric must have a symmetric spatial wave function.

$$\psi_{TOTAL} = \psi_{symmetric} \, \chi_{antisymmetric}$$

antisymmetric




# <u>Atoms</u>

1. A neutral atom of atomic number $Z$ consists of a heavy nucleus with electric charge $Ze$ surrounded by $Z$ electrons each with charge $-e$

2. The Hamiltonian for this system

$$H = \sum_{j=1}^{Z} \left\{ \frac{-\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\varepsilon_0}\right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\right) \sum_{j \neq k}^{Z} \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

$H\psi = E\psi$ T.I. Schrödinger Equation
to get the eigenfunction for $Z$ electrons.

# Helium Atom

$Z = 2$

$$H = \left\{ \frac{-\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ \frac{-\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r^2} \right\} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

If we ignored the last term, we would have 2 electrons that interact only with the nucleus and we could write the total wavefunction as:

$$\psi_{TOTAL}(\vec{r}_1, \vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\, \psi_{n'\ell' m'}(\vec{r}_2)$$

where the total energy of the 2 electrons is:

$$E_n + E_{n'} = \frac{-13.6\text{ eV } Z^2}{n^2} - \frac{13.6\text{ eV } Z^2}{n'^2}$$

for $Z = 2$ and $n = n' = 1$ "the ground state"

$$\boxed{E_n + E_{n'} = -108.8\text{ eV}}$$ non-interacting electrons.

The ground state w.f. would be:

$$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\, \psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1 + r_2)/a_0}$$

$\psi_0 \Rightarrow$ is a symmetric wave function. Since both $e^-$'s are in the same $n\,\ell\,m$ state, their combined spin angular momentum must be <u>antisymmetric</u>. So, the ground state of He must have electrons in a singlet state.

$$\boxed{E_0\ (\text{measured}) = -78.975\text{ eV}}$$

Homework - Griffiths problem 5.9 Both $e^-$s in the $n=2$ state
KE=? for the ejected $e^-$?
Assume non-interacting electrons. Part b, find a general equation for $\frac{1}{\lambda} = ?$

**Table 7-2** Some Eigenfunctions for the One-Electron Atom

| Quantum Numbers $n$ | $l$ | $m_l$ | Eigenfunctions |
|---|---|---|---|
| 1 | 0 | 0 | $\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$ |
| 2 | 0 | 0 | $\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$ |
| 2 | 1 | 0 | $\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\theta$ |
| 2 | 1 | $\pm 1$ | $\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\sin\theta\, e^{\pm i\varphi}$ |
| 3 | 0 | 0 | $\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$ |
| 3 | 1 | 0 | $\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\cos\theta$ |
| 3 | 1 | $\pm 1$ | $\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\sin\theta\, e^{\pm i\varphi}$ |
| 3 | 2 | 0 | $\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta-1)$ |
| 3 | 2 | $\pm 1$ | $\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin\theta\cos\theta\, e^{\pm i\varphi}$ |
| 3 | 2 | $\pm 2$ | $\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin^2\theta\, e^{\pm 2i\varphi}$ |

Griffiths Problem 5.11 ** Work this out.

Calculate $\left\langle \frac{1}{|\vec{r}_1-\vec{r}_2|} \right\rangle$ for $\psi_0 = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)$ ~~Hydrogen~~ Helium

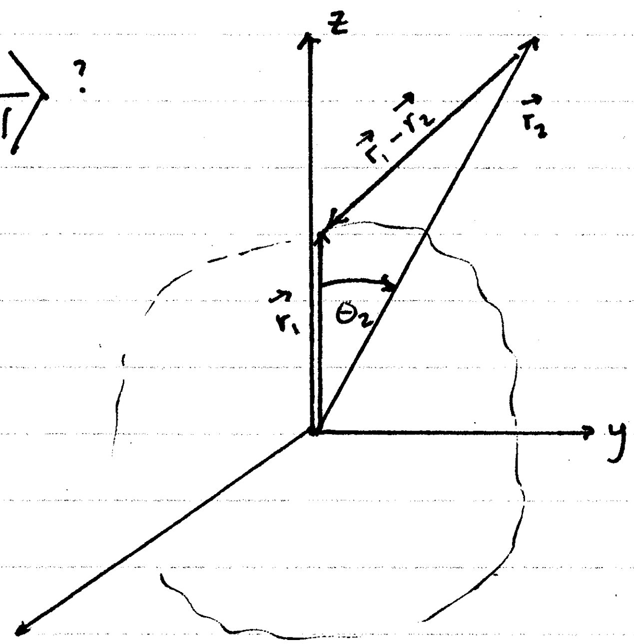
1.) Do the $d^3 r_2$ integral first using spherical coordinates

2.) Set $\vec{r}_1$ along the polar axis where

$$|\vec{r}_1-\vec{r}_2| = \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}$$

3.) The $r_2$ integration will have to be broken up into 2 pieces

$$\int_0^\infty dr_2 \rightarrow \int_0^{r_1} dr_2 + \int_{r_1}^\infty dr_2$$




Why do we want to calculate $\left\langle \frac{1}{|\vec{r}_1-\vec{r}_2|} \right\rangle$ ?

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 + V(\vec{r}_1) - \frac{\hbar^2}{2m}\nabla_2^2 + V(\vec{r}_2) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}$$

$E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle$ Eq. 3.13 Griffiths

$$E_0 = \underbrace{\left\langle \psi_0 \middle| -\frac{\hbar^2}{2m}\nabla_1^2 + V(\vec{r}_1) \middle| \psi_0 \right\rangle}_{-54.4\text{ eV}} + \underbrace{\left\langle \psi_0 \middle| \frac{-\hbar^2}{2m}\nabla_2^2 + V(\vec{r}_2) \middle| \psi_0 \right\rangle}_{-54.4\text{ eV}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\left\langle \psi_0 \middle| \frac{1}{|\vec{r}_1-\vec{r}_2|} \middle| \psi_0 \right\rangle}_{+\ ??\ \text{solve for this.}}$$

$$\psi_0 = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 e^{-\frac{Z}{a_0}(r_1+r_2)}$$

$$\psi_0 = \frac{1}{\pi}\frac{8}{a_0^3} e^{-\frac{2}{a_0}(r_1+r_2)}$$

$Z=2$

So, let's calculate $\frac{e^2}{4\pi\varepsilon_0} \langle \psi_0 | \frac{1}{|\vec{r}_1-\vec{r}_2|} | \psi_0 \rangle = \left\langle \frac{1}{|\vec{r}_1 - r_2|} \right\rangle \frac{e^2}{4\pi\varepsilon_0} = \frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle$

$$\left\langle \frac{1}{|\vec{r}_1-\vec{r}_2|} \right\rangle = \langle \psi_0 | \frac{1}{|\vec{r}_1-\vec{r}_2|} | \psi_0 \rangle$$

$$\left\langle \frac{1}{|\vec{r}_1-\vec{r}_2|} \right\rangle = \int d^3\vec{r}_1 \int d^3\vec{r}_2 \; \psi_0^* \psi_0 \frac{1}{|\vec{r}_1-\vec{r}_2|}$$

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty 4\pi r_1^2 \, dr_1 \int_0^\infty 2\pi r_2^2 \, dr_2 \left(\frac{8}{\pi a_0^3}\right)^2 e^{-\frac{4}{a_0}(r_1+r_2)} \int_0^\pi d\theta_2 \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}$$

Using Mathematica:

$$\int_0^\pi d\theta_2 \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} = \begin{cases} \frac{2}{r_1} & \text{for } r_2 < r_1 \\ \frac{2}{r_2} & \text{for } r_2 > r_1 \end{cases}$$

$$\left\langle \frac{1}{r} \right\rangle = \left(\frac{8}{\pi a_0^3}\right)^2 2\pi \; 4\pi \int_0^\infty e^{-\frac{4r_1}{a_0}} \left\{ \int_0^{r_1} r_2^2 \left(\frac{2}{r_1}\right) e^{-\frac{4r_2}{a_0}} dr_2 + \int_{r_1}^\infty r_2^2 \left(\frac{2}{r_2}\right) e^{-\frac{4r_2}{a_0}} dr_2 \right\} r_1^2 \, dr_1$$

$$\boxed{\left\langle \frac{1}{r} \right\rangle = \frac{5}{4a_0}}$$ using Mathematica

b.) Estimate the $\frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle$ contribution.

$$\frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle = \left(\frac{e^2}{4\pi\varepsilon_0 \hbar c}\right) \hbar c \left(\frac{5}{4a_0}\right) = \alpha \frac{5\hbar c}{4a_0} = \frac{1}{137} \frac{5\,(197\text{ eV}\cdot\text{nm})}{4\,(0.0529\text{ nm})} = \underline{\underline{33.97\text{ eV}}}$$

# Helium

$$E_0 + V_{ee} = (-109 + 34)\,eV = \underline{\underline{-75\ eV}}$$

Certainly closer to the −79 eV measured by experiment.
We're still working with an approximate w.f.

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What do the energy levels of He look like?

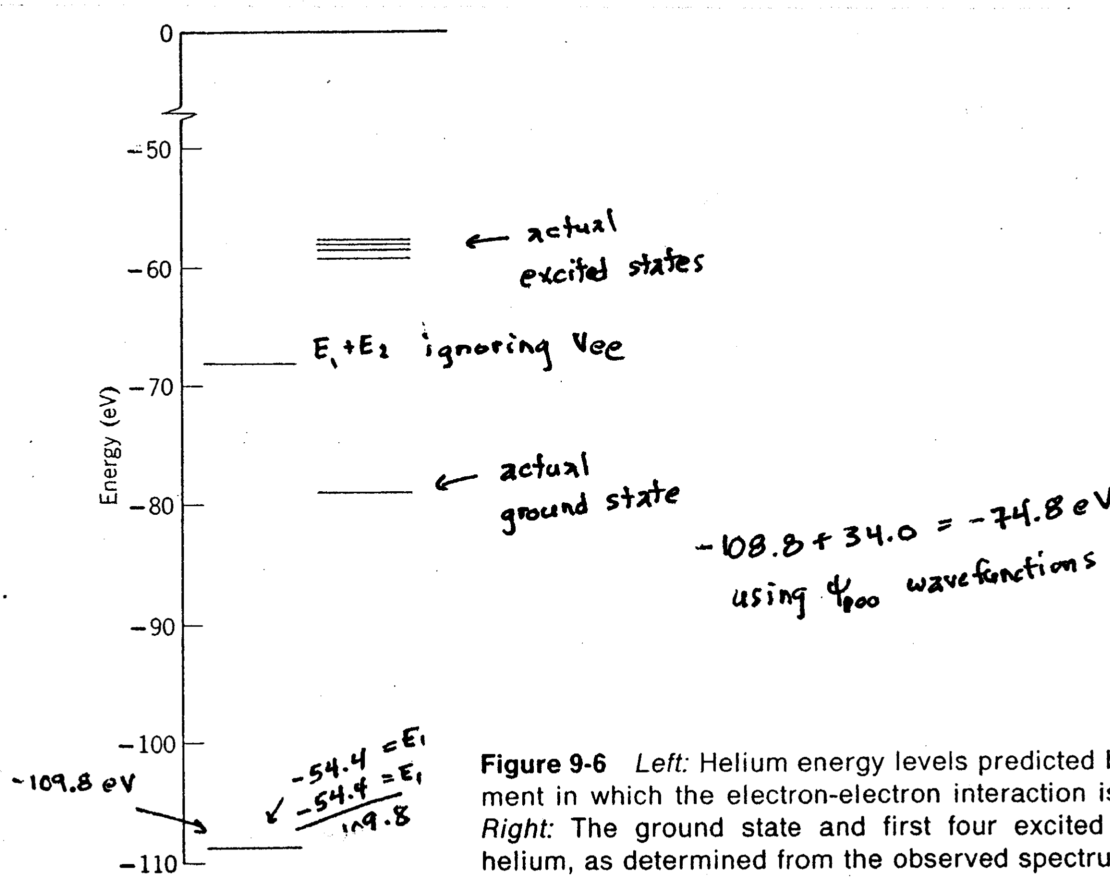


**Figure 9-6** *Left:* Helium energy levels predicted by a treatment in which the electron-electron interaction is ignored. *Right:* The ground state and first four excited states of helium, as determined from the observed spectrum.

# Helium



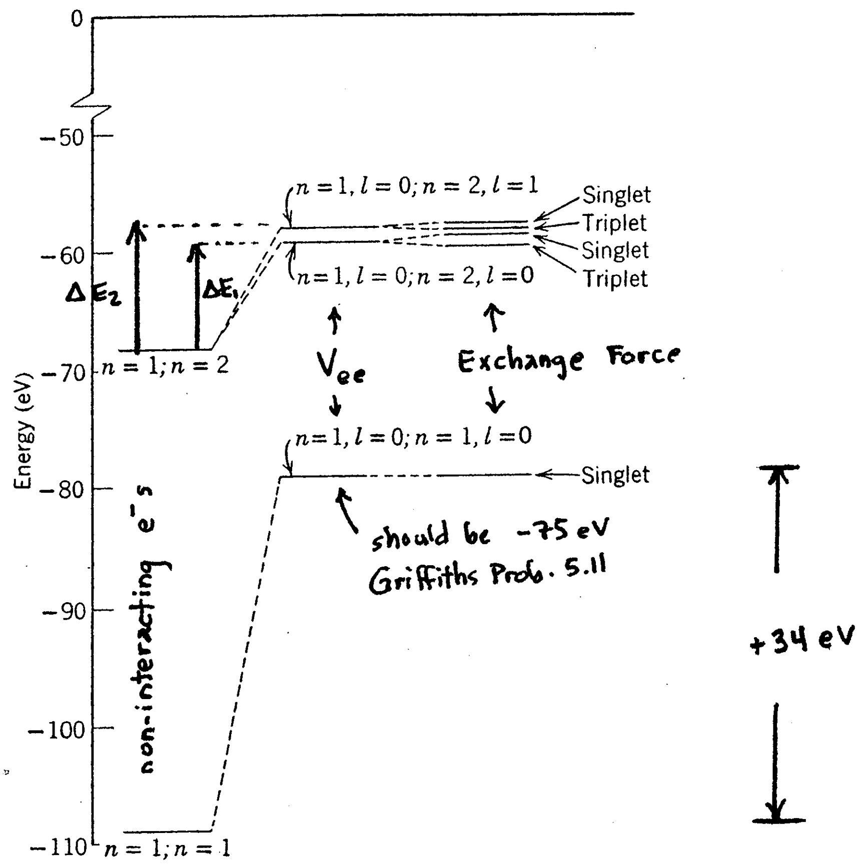


**Figure 9-7** The low-lying energy levels of helium. *Left:* The levels that would be found if there were no Coulomb interaction between its electrons. *Center:* The levels that would be found if there were a Coulomb interaction but no exchange force. *Right:* The levels that would be found if there were a Coulomb interaction and an exchange force. These levels are in excellent agreement with the experimentally observed levels shown on the right in Figure 9-6.

**Homework:** Calculate the shift in energy in the above figure for

1. $n=1;\ n=2 \rightarrow n=1, \ell=0;\ n=2, \ell=0$ <u>and</u>
2. $n=1;\ n=2 \rightarrow n=1, \ell=0;\ n=2, \ell=1$

From Mathematica

See pages 24 & 25

1. $\cancel{\psi_{TOTAL} = \psi_{100}(\vec{r}_1)\,\psi_{200}(\vec{r}_2)}$ $\quad\cancel{\Delta E_1 = 11.407 \text{ eV}}$
2. $\cancel{\psi_{TOTAL} = \psi_{100}(\vec{r}_1)\,\psi_{210}(\vec{r}_2)}$ $\quad\cancel{\Delta E_2 = 14.392 \text{ eV}}$ $\Big\}$ $\underline{2.98 \text{ eV}}$

As before, calculate the $\int d\Theta_2$ integral for $\underline{r_1 < r_2}$ and $\underline{r_2 < r_1}$

# One electron atoms

▲ = location of $\langle r_{n\ell} \rangle$

$P_{n\ell}(r)\,dr = \underbrace{R^*_{n\ell}(r)\,R_{n\ell}(r)\;4\pi r^2}_{\text{plotted below}}\,dr$

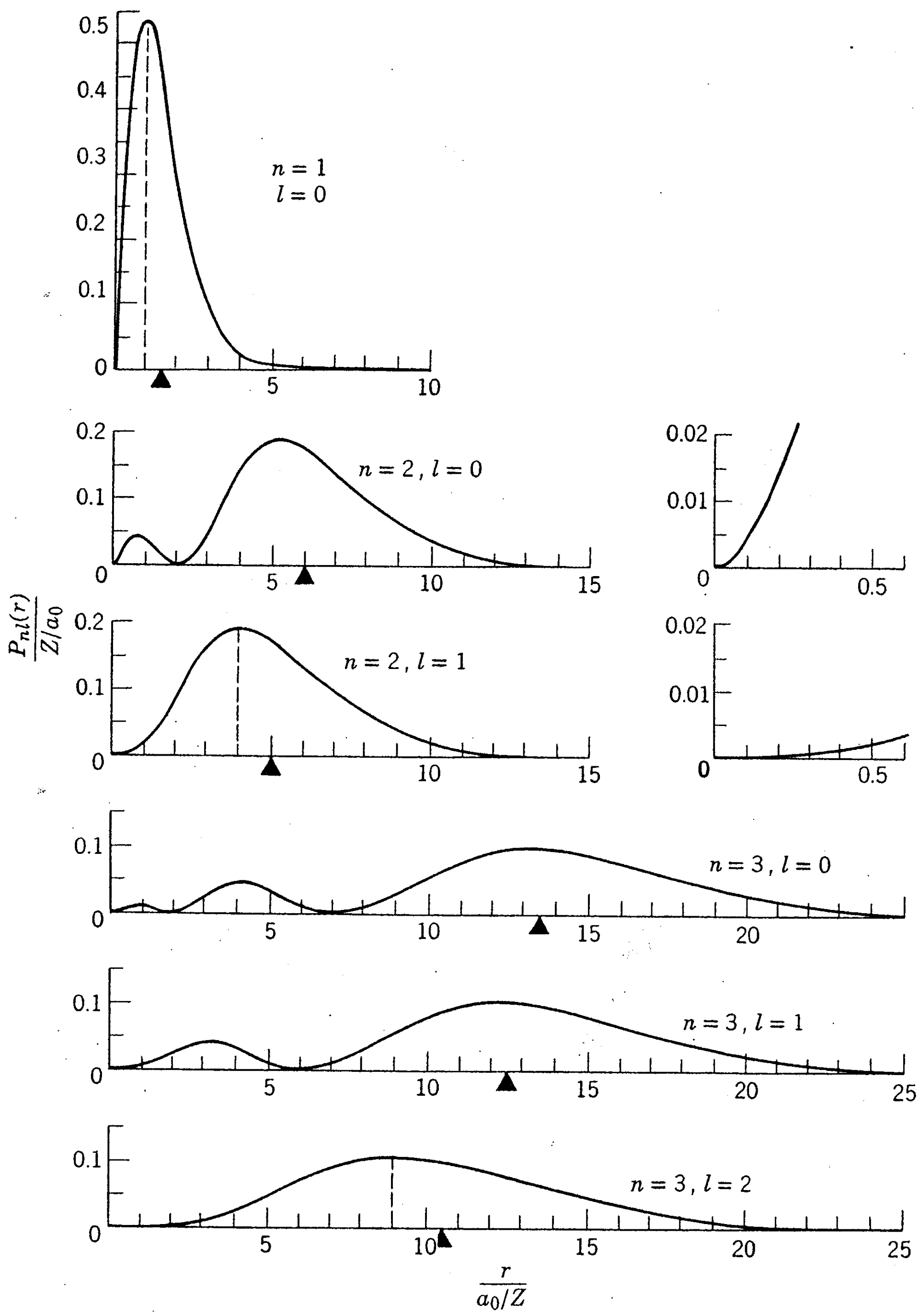


**Figure 7-5** The radial probability density for the electron in a one-electron atom for $n = 1, 2, 3$ and the values of $l$ shown. The triangle on each abscissa indicates the value of $\overline{r_{nl}}$ as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{\max} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{\text{Bohr}} = n^2 a_0/Z$, which is indicated by the location of the dashed line.

$$\langle r_{n\ell} \rangle = \int_0^\infty r \; P_{n\ell}(r) \; dr \;\; = \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2}\left[ 1 - \frac{\ell(\ell+1)}{n^2} \right] \right\}$$

<u>Conclusion</u>: Larger $\ell$ for a given principle quantum number $n$, means $\langle r_{n\ell} \rangle$ is smaller $\Rightarrow$ larger energy shift.

# Back to Helium

<u>Finally</u>, the Exchange Force

The singlet states are higher in energy compared to the triplet states

Why?

Singlet $\rightarrow$ antisymmetric $\quad \psi_{TOTAL}$ = must be antisymmetric

$$\psi_{TOTAL} = \psi_{spatial} \, \chi_{spin} = \psi_{spatial}(\text{symmetric}) \, \chi_{spin}(\text{antisymmetric})$$

singlet

$\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

$\psi_{spatial}$ (symmetric) $\rightarrow$ means the electrons are "closer" so the $V_{ee}$ correction is "higher"

So, both singlet states in ($\ell = 0$ and $\ell = 1$) have singlet states that are higher in energy compared to their respective triplet states.

Page 21 continued:

Homework Problem Cont'd:

① $n=1$ ; $n=2$ $\longrightarrow$ $n=1,\ \ell=0$ ; $n=2,\ \ell=0$

$$\psi_S(r_1, r_2) = \frac{1}{\sqrt{2}}\left\{ \psi_{100}(r_1)\,\psi_{200}(r_2) + \psi_{100}(r_2)\,\psi_{200}(r_1) \right\} \times \chi_{spin}^{singlet}$$

$$\psi_A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left\{ \psi_{100}(r_1)\,\psi_{200}(r_2) - \psi_{100}(r_2)\,\psi_{200}(r_1) \right\} \times \chi_{spin}^{triplet}$$

If we ignore the Vee interaction, then $E_{TOTAL} = E_1 + E_2$

$$= -\frac{1}{2}\,\frac{mc^2\alpha^2 Z^2}{(n=1)^2} + \left( -\frac{1}{2}\, \frac{mc^2\alpha^2 Z^2}{(n=2)^2} \right) = -54.4\text{ eV} \; -13.6\text{ eV}$$

$E_{TOTAL} = -68$ eV