



UNIVERSITY OF
CAMBRIDGE

NST Part II Physics
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ADVANCED QUANTUM PHYSICS

Handout 6

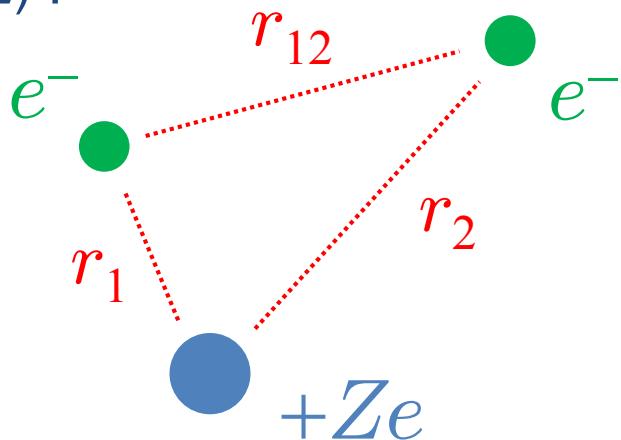
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- ▶ Identical particles
 - ▶ Spin and statistics (fermions and bosons)
 - ▶ Exchange forces
 - ▶ The Helium atom

Identical Particles

- The next element after hydrogen is *helium* ($Z = 2$) :

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}} \right)$$

$$\hat{H}(1, 2) = \hat{H}(2, 1)$$



We encounter a new feature

→ the helium atom contains two identical (indistinguishable) electrons

- In writing the Hamiltonian, H , we assign labels “1” and “2” to the electron parameters, but these are just “dummy” mathematical indices
 - they are not attached to any *particular* electron
 - interchanging the labels $1 \leftrightarrow 2$ leaves the Hamiltonian H unchanged

Identical particles (2)

- In classical mechanics we can (in principle) keep track of each electron separately
 - they are effectively distinguishable

In quantum mechanics, this is not possible – we cannot distinguish between identical particles or follow their individual trajectories

- Specifically, the quantity

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

is the probability of finding one electron in the volume $d^3\mathbf{r}_1$ at position \mathbf{r}_1 and the other electron in the volume $d^3\mathbf{r}_2$ at position \mathbf{r}_2

The equivalent quantity with the labels $1 \leftrightarrow 2$ interchanged,

$$|\psi(\mathbf{r}_2, \mathbf{r}_1)|^2 d^3\mathbf{r}_2 d^3\mathbf{r}_1$$

has exactly the same interpretation; hence

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

All this has profound consequences ...

Identical Particle Exchange

- Consider a system of N particles, and write the possible states of the system generically as

$$|\psi\rangle = |1, 2, 3, \dots, N\rangle$$

The labels 1, 2, 3, ... represent both the internal (e.g. spin) and external (e.g. position) degrees of freedom of each particle

e.g. the label “3” represents $\{ \mathbf{r}_3, \mathbf{p}_3, s_3, m_{s3}, \ell_3, m_{\ell3}, \dots \}$

- Suppose the labels j and k correspond to a pair of identical particles (e.g. two electrons, or two protons)

Then the pair of states related by interchange of the labels j and k are physically indistinguishable and can differ by at most a phase factor :

$$|1, 2, \dots, j, \dots, k, \dots, N\rangle = e^{i\phi} |1, 2, \dots, k, \dots, j, \dots, N\rangle \quad (6.4.1)$$

- Interchanging the labels j and k throughout the equation above gives

$$|1, 2, \dots, k, \dots, j, \dots, N\rangle = e^{i\phi} |1, 2, \dots, j, \dots, k, \dots, N\rangle \quad (6.4.2)$$

Identical particle exchange (2)

- Combining equations (6.4.1) and (6.4.2), we then obtain

$$|1, 2, \dots, j, \dots, k, \dots, N\rangle = e^{2i\phi} |1, 2, \dots, j, \dots, k, \dots, N\rangle$$

Hence we must have

$$e^{2i\phi} = 1 ; \quad e^{i\phi} = \pm 1$$

- Thus, interchanging the labels associated with identical particles can change the state of the system by at most a sign :

$$|1, 2, \dots, k, \dots, j, \dots, N\rangle = \pm |1, 2, \dots, j, \dots, k, \dots, N\rangle \quad (6.5.2)$$

- If the "+" sign applies,

$$|1, 2, \dots, k, \dots, j, \dots, N\rangle = |1, 2, \dots, j, \dots, k, \dots, N\rangle$$

then wavefunctions are *symmetric* under particle interchange, and the particles are (by definition) **bosons**

(and obey Bose-Einstein statistics for large N)

Identical particle exchange (3)

- If the “–” sign applies,

$$|1, 2, \dots, k, \dots, j, \dots, N\rangle = -|1, 2, \dots, j, \dots, k, \dots, N\rangle$$

then wavefunctions are *antisymmetric* under particle interchange, and the particles are (by definition) **fermions**

(and obey Fermi-Dirac statistics for large N)

- For fermions, setting $k = j$ above gives

$$|1, 2, \dots, j, \dots, j, \dots, N\rangle = 0$$

Hence two identical fermions cannot occupy a state where they are both assigned an identical set of quantum numbers

→ the ***Pauli exclusion principle***

e.g. two identical fermions in the same spin state can not occupy the same spatial state (and *vice versa*) (if all other qu. nos. are the same)

- But how do we know which particles are fermions and which are bosons ?

Spin and Statistics

- Spin and statistics are intimately connected :
 - any particle with *integer* spin is a *boson*
 - any particle with *half-integer* spin is a *fermion*
 - In non-relativistic quantum mechanics, this connection between spin and statistics must be accepted as an empirical observation
- In quantum field theory, this connection can be formally established
- the ***spin-statistics theorem***
- The connection between spin and statistics is consistent with the addition of angular momentum in quantum mechanics (as we now show)
 - i.e. it applies consistently both to single particles (electrons, muons, ...) and to composite, multi-particle systems (protons, neutrons, nuclei, atoms, molecules, ...)

Spin and statistics (2)

- For a multi-particle system, the total angular momentum operator is

$$\hat{\mathbf{J}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \dots + \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2 + \dots$$

The total angular momentum quantum number j can take on a range of values given by

$$j = s_1 \otimes s_2 \otimes \cdots \otimes \ell_1 \otimes \ell_2 \otimes \cdots$$

$\underbrace{\hspace{1cm}}$ $\underbrace{\hspace{1cm}}$

$$(s_i = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots) \quad (\ell_i = 0, 1, 2, \dots)$$

- Whether the quantum number j is integer or half-integer depends *only* on the number of particles with half-integer spin :

even # of half-integer spin particles $\Rightarrow j$ is integer

odd # of half-integer spin particles $\Rightarrow j$ is half-integer

e.g. $\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} \otimes 1 = 0, 1, 2, 3$ (all integer)

$$\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} \otimes 1 \otimes 1 = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$$
 (all half-integer)

Spin and statistics (3)

- Now consider the statistics of a composite system ...
 - e.g. consider a system containing two protons, each of which contains two u ("up") quarks and a d ("down") quark, in an identical state :

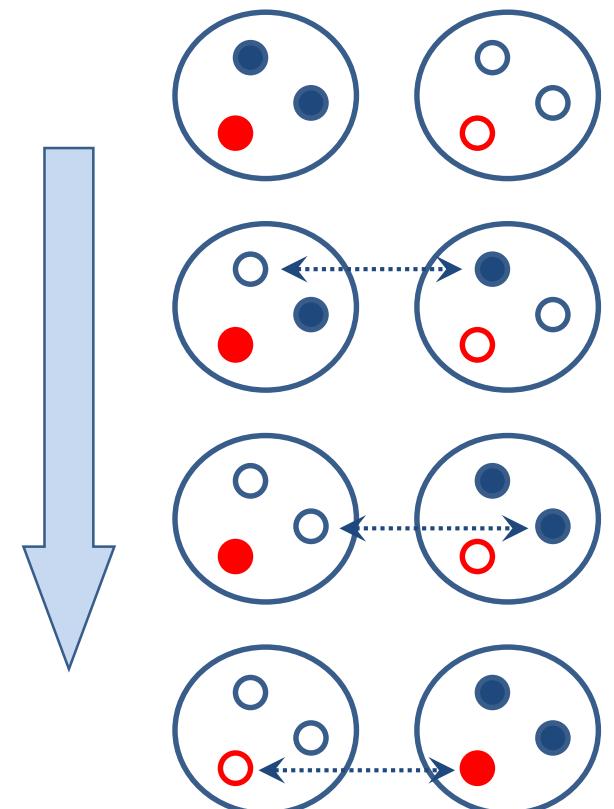
$$|\psi\rangle = |\dots; u_1, u_2, d; \dots; u'_1, u'_2, d' ; \dots\rangle$$

- Exchange the two protons, quark by quark :

$$\begin{aligned} |\psi\rangle &= +|..., u_1, u_2, d, \dots, u'_1, u'_2, d', \dots\rangle \\ &= -|..., u'_1, u_2, d, \dots, u_1, u'_2, d', \dots\rangle \\ &= +|..., u'_1, u'_2, d, \dots, u_1, u_2, d', \dots\rangle \\ &= -|..., u'_1, u'_2, d', \dots, u_1, u_2, d, \dots\rangle \end{aligned}$$

- We obtain an overall “–” sign
 - (as a consequence of there being an odd number of interchanges of identical fermions)

Hence a proton is a *fermion*



Spin and statistics (4)

- Now interchange two ${}^4\text{He}$ atoms, each of which contains (p, p, n, n, e^-, e^-) :

$$\begin{aligned} |\psi\rangle &= +|p_1, p_2, n_1, n_2, e_1, e_2, p'_1, p'_2, n'_1, n'_2, e'_1, e'_2\rangle \\ &= -|p'_1, p_2, n_1, n_2, e_1, e_2, p_1, p'_2, n'_1, n'_2, e'_1, e'_2\rangle \\ &= +|p'_1, p'_2, n_1, n_2, e_1, e_2, p_1, p_2, n'_1, n'_2, e'_1, e'_2\rangle \\ &= \dots \quad \dots \\ &= +|p'_1, p'_2, n'_1, n'_2, e'_1, e'_2, p_1, p_2, n_1, n_2, e_1, e_2\rangle \end{aligned}$$

We now obtain an overall “+” sign, so a ${}^4\text{He}$ atom is a *boson*

Thus, a composite particle containing an even (odd) number of fermions is a boson (fermion)

- From slide 6.8, a system containing an even (odd) number of half-integer spin particles has integer (half-integer) total spin

So, for composite particles, just as for single particles :

<i>integer spin</i>	\Leftrightarrow	<i>boson</i>
<i>half-integer spin</i>	\Leftrightarrow	<i>fermion</i>

Systems of Identical Particles

- For a system of N identical *non-interacting* particles, the Hamiltonian can be expressed as a sum of N identical single-particle Hamiltonians :

$$\hat{H}(1, 2, \dots, N) = \sum_{i=1}^N \hat{H}_1(i)$$

- Each single-particle Hamiltonian H_1 possesses a common (possibly infinite) set of eigenstates, which can be listed as

$$\hat{H}_1|\alpha\rangle = E(\alpha)|\alpha\rangle, \quad \hat{H}_1|\beta\rangle = E(\beta)|\beta\rangle, \quad \dots$$

Then an N -particle state of the form

$$|\psi\rangle = |1, \alpha_1\rangle|2, \alpha_2\rangle\dots|N, \alpha_N\rangle ; \quad \alpha_j \in \{\alpha, \beta, \dots\}$$

is an eigenstate of the N -particle Hamiltonian, with energy eigenvalue

$$E = \sum_{i=1}^N E(\alpha_i)$$

Systems of identical particles (2)

- To show this :

$$\begin{aligned}\hat{H}(1, 2, \dots, N)|\psi\rangle &= \left(\sum_i \hat{H}_1(i) \right) |1, \alpha_1\rangle |2, \alpha_2\rangle \dots |N, \alpha_N\rangle \\ &= \sum_i |1, \alpha_1\rangle |2, \alpha_2\rangle \dots [\hat{H}_1(i)|i, \alpha_i\rangle] \dots |N, \alpha_N\rangle \\ &= \sum_i |1, \alpha_1\rangle |2, \alpha_2\rangle \dots [E(\alpha_i)|i, \alpha_i\rangle] \dots |N, \alpha_N\rangle \\ &= \left(\sum_i E(\alpha_i) \right) |\psi\rangle = E|\psi\rangle\end{aligned}$$

- However states of the form $|\psi\rangle = |1, \alpha_1\rangle |2, \alpha_2\rangle \dots |N, \alpha_N\rangle$ are in general neither symmetric nor antisymmetric under particle interchange
 - ⇒ a *single* product state of this form cannot, in general, be used directly to describe a system of N identical particles

But linear combinations of these product states can be formed which *do* have definite symmetry ...

Slater determinants

- For a system consisting of $N = 2$ identical fermions, consider a state of the form

$$|\psi\rangle_A = \frac{1}{\sqrt{2}}(|1, \alpha\rangle|2, \beta\rangle - |1, \beta\rangle|2, \alpha\rangle)$$

Under interchange $1 \leftrightarrow 2$ of the particle labels, this state transforms to

$$|\psi\rangle'_A = \frac{1}{\sqrt{2}}(|2, \alpha\rangle|1, \beta\rangle - |2, \beta\rangle|1, \alpha\rangle) = -|\psi\rangle_A$$

The state $|\psi\rangle_A$ is therefore *antisymmetric* under particle interchange, and can serve as a valid state of the system for two identical fermions

- This two-particle state can be written in the form of a determinant as

$$|\psi\rangle_A = \frac{1}{\sqrt{2}} \begin{vmatrix} |1, \alpha\rangle & |2, \alpha\rangle \\ |1, \beta\rangle & |2, \beta\rangle \end{vmatrix}$$

or equivalently, adjusting the notation, as

$$|\psi\rangle_A = \frac{1}{\sqrt{2}} \begin{vmatrix} |1, \alpha_1\rangle & |2, \alpha_1\rangle \\ |1, \alpha_2\rangle & |2, \alpha_2\rangle \end{vmatrix} \quad \begin{cases} |\alpha_1\rangle \equiv |\alpha\rangle \\ |\alpha_2\rangle \equiv |\beta\rangle \end{cases}$$

Slater determinants

- For N identical fermions, this extends to

$$|\psi\rangle_A = \frac{1}{\sqrt{N!}} \begin{vmatrix} |1, \alpha_1\rangle & |2, \alpha_1\rangle & \dots & |N, \alpha_1\rangle \\ |1, \alpha_2\rangle & |2, \alpha_2\rangle & \dots & |N, \alpha_2\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |1, \alpha_N\rangle & |2, \alpha_N\rangle & \dots & |N, \alpha_N\rangle \end{vmatrix}$$

where the right-hand side is known as a *Slater determinant*

- A Slater determinant has all the properties required for identical fermions :

- Interchange of the labels assigned to any two particles is equivalent to the interchange of two columns, and gives a change of sign :

$$|\psi\rangle_A \longrightarrow -|\psi\rangle_A$$

- If any two rows are the same (equivalent to having two particles in the same single-particle state) the determinant vanishes :

$$|\psi\rangle_A = 0$$

Slater determinants (2)

- Now consider identical *bosons* rather than identical fermions

For a system consisting of $N = 2$ identical bosons, we can construct a symmetric state using only one single-particle state $|\alpha\rangle$:

$$|\psi\rangle_S = |1, \alpha\rangle |2, \alpha\rangle$$

Hence, unlike the case for identical fermions, two identical bosons can both occupy the *same* single-particle state

- Two identical bosons can also occupy *different* single-particle states, in which case the state of the system must be

$$|\psi\rangle_S = \frac{1}{\sqrt{2}} (|1, \alpha\rangle |2, \beta\rangle + |1, \beta\rangle |2, \alpha\rangle)$$

The above states are *symmetric* under particle interchange $1 \leftrightarrow 2$

e.g. $|\psi\rangle'_S = \frac{1}{\sqrt{2}} (|2, \alpha\rangle |1, \beta\rangle + |2, \beta\rangle |1, \alpha\rangle) = |\psi\rangle_S$

Slater determinants (3)

- To extend this to $N > 2$ identical bosons, multiply out the Slater determinant and set the sign of every term to be positive :

For example, for $N = 3$, the Slater determinant is

$$|\psi\rangle_A = \frac{1}{\sqrt{3!}} \begin{vmatrix} |1, \alpha_1\rangle & |2, \alpha_1\rangle & |3, \alpha_1\rangle \\ |1, \alpha_2\rangle & |2, \alpha_2\rangle & |3, \alpha_2\rangle \\ |1, \alpha_3\rangle & |2, \alpha_3\rangle & |3, \alpha_3\rangle \end{vmatrix}$$

- For *fermions*, this gives the totally *antisymmetric* state

$$\begin{aligned} \sqrt{6} |\psi\rangle_A = & |1, \alpha_1\rangle |2, \alpha_2\rangle |3, \alpha_3\rangle - |1, \alpha_1\rangle |2, \alpha_3\rangle |3, \alpha_2\rangle + |1, \alpha_2\rangle |2, \alpha_3\rangle |3, \alpha_1\rangle \\ & - |1, \alpha_2\rangle |2, \alpha_1\rangle |3, \alpha_3\rangle + |1, \alpha_3\rangle |2, \alpha_1\rangle |3, \alpha_2\rangle - |1, \alpha_3\rangle |2, \alpha_2\rangle |3, \alpha_1\rangle \end{aligned}$$

(antisymmetric under all interchanges $1 \leftrightarrow 2$, $1 \leftrightarrow 3$, $2 \leftrightarrow 3$)

- For *bosons*, set all signs to “+” to construct the totally *symmetric* state

$$\begin{aligned} \sqrt{6} |\psi\rangle_S = & |1, \alpha_1\rangle |2, \alpha_2\rangle |3, \alpha_3\rangle + |1, \alpha_1\rangle |2, \alpha_3\rangle |3, \alpha_2\rangle + |1, \alpha_2\rangle |2, \alpha_3\rangle |3, \alpha_1\rangle \\ & + |1, \alpha_2\rangle |2, \alpha_1\rangle |3, \alpha_3\rangle + |1, \alpha_3\rangle |2, \alpha_1\rangle |3, \alpha_2\rangle + |1, \alpha_3\rangle |2, \alpha_2\rangle |3, \alpha_1\rangle \end{aligned}$$

Two-Electron Systems

- Consider a two-electron system where both electrons occupy the *same spatial state* $|a(\mathbf{r})\rangle$; there are then two available single-particle states :

$$|a\uparrow\rangle = \psi_a(\mathbf{r})|\uparrow\rangle \equiv |a(\mathbf{r})\rangle|\uparrow\rangle \equiv |a\rangle|\uparrow\rangle$$

$$|a\downarrow\rangle = \psi_a(\mathbf{r})|\downarrow\rangle \equiv |a(\mathbf{r})\rangle|\downarrow\rangle \equiv |a\rangle|\downarrow\rangle$$

- If both electrons also occupy the same *spin state*,

$$|1, a\uparrow\rangle|2, a\uparrow\rangle \quad \text{or} \quad |1, a\downarrow\rangle|2, a\downarrow\rangle$$

then it is *not possible* to form an overall antisymmetric wavefunction; the Slater determinants vanish :

$$|\psi\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} |1, a\uparrow\rangle & |2, a\uparrow\rangle \\ |1, a\uparrow\rangle & |2, a\uparrow\rangle \end{vmatrix} = 0 ; \quad |\psi\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} |1, a\downarrow\rangle & |2, a\downarrow\rangle \\ |1, a\downarrow\rangle & |2, a\downarrow\rangle \end{vmatrix} = 0$$

(an example of the Pauli exclusion principle: the two electrons cannot occupy the same spatial state *and* the same spin state)

Two-electron systems (2)

- The only two-electron wavefunction consistent with the Pauli principle is

$$\begin{aligned} |\psi\rangle &= \frac{1}{\sqrt{2}} \begin{vmatrix} |1, a\uparrow\rangle & |2, a\uparrow\rangle \\ |1, a\downarrow\rangle & |2, a\downarrow\rangle \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (|1, a\uparrow\rangle|2, a\downarrow\rangle - |1, a\downarrow\rangle|2, a\uparrow\rangle) \\ &= \frac{1}{\sqrt{2}} (|a\rangle_1|\uparrow\rangle_1|a\rangle_2|\downarrow\rangle_2 - |a\rangle_1|\downarrow\rangle_1|a\rangle_2|\uparrow\rangle_2) \end{aligned}$$

This requires the electrons to occupy *different* spin states

- The two-electron wavefunction above can be written as a product of separate spatial and (singlet) spin factors as

$$|\psi\rangle = |a\rangle_1|a\rangle_2 \times \frac{1}{\sqrt{2}} (|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2)$$

(symmetric)

(antisymmetric)

Thus, for two identical spin-half particles in the same spatial state, the total spin of the system *must* be $S = 0$

Two-electron systems (3)

- Now suppose the electrons are in *distinct* spatial states, $|a(\mathbf{r})\rangle$ and $|b(\mathbf{r})\rangle$

Then two new single-particle states become available :

$$|b\uparrow\rangle = \psi_b(\mathbf{r})|\uparrow\rangle \equiv |b(\mathbf{r})\rangle|\uparrow\rangle \equiv |b\rangle|\uparrow\rangle$$

$$|b\downarrow\rangle = \psi_b(\mathbf{r})|\downarrow\rangle \equiv |b(\mathbf{r})\rangle|\downarrow\rangle \equiv |b\rangle|\downarrow\rangle$$

- It is now possible to form *four* non-zero Slater determinants :

$$|\psi\rangle_{\uparrow\uparrow} = \frac{1}{\sqrt{2}} \begin{vmatrix} |1, a\uparrow\rangle & |2, a\uparrow\rangle \\ |1, b\uparrow\rangle & |2, b\uparrow\rangle \end{vmatrix} = \frac{1}{\sqrt{2}} (|1, a\uparrow\rangle|2, b\uparrow\rangle - |1, b\uparrow\rangle|2, a\uparrow\rangle)$$

$$|\psi\rangle_{\downarrow\downarrow} = \frac{1}{\sqrt{2}} \begin{vmatrix} |1, a\downarrow\rangle & |2, a\downarrow\rangle \\ |1, b\downarrow\rangle & |2, b\downarrow\rangle \end{vmatrix} = \frac{1}{\sqrt{2}} (|1, a\downarrow\rangle|2, b\downarrow\rangle - |1, b\downarrow\rangle|2, a\downarrow\rangle)$$

$$|\psi\rangle_{\uparrow\downarrow} = \frac{1}{\sqrt{2}} \begin{vmatrix} |1, a\uparrow\rangle & |2, a\uparrow\rangle \\ |1, b\downarrow\rangle & |2, b\downarrow\rangle \end{vmatrix} = \frac{1}{\sqrt{2}} (|1, a\uparrow\rangle|2, b\downarrow\rangle - |1, b\downarrow\rangle|2, a\uparrow\rangle)$$

$$|\psi\rangle_{\downarrow\uparrow} = \frac{1}{\sqrt{2}} \begin{vmatrix} |1, a\downarrow\rangle & |2, a\downarrow\rangle \\ |1, b\uparrow\rangle & |2, b\uparrow\rangle \end{vmatrix} = \frac{1}{\sqrt{2}} (|1, a\downarrow\rangle|2, b\uparrow\rangle - |1, b\uparrow\rangle|2, a\downarrow\rangle)$$

Two-electron systems (4)

- For the first two of these, the two-particle system is in an eigenstate of total spin, $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$, with $S = 1$:

$$|\psi\rangle_{\uparrow\uparrow} = \frac{1}{\sqrt{2}}(|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2) \times |\uparrow\rangle_1|\uparrow\rangle_2 \quad (S = 1, m_S = +1)$$

$$|\psi\rangle_{\downarrow\downarrow} = \frac{1}{\sqrt{2}}(|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2) \times |\downarrow\rangle_1|\downarrow\rangle_2 \quad (S = 1, m_S = -1)$$

- For the remaining two Slater determinants, the linear combinations

$$|\psi\rangle_{\pm} = \frac{1}{\sqrt{2}}(|\psi\rangle_{\uparrow\downarrow} \pm |\psi\rangle_{\downarrow\uparrow})$$

can be factorised into separate spatial and spin components :

$$|\psi\rangle_{-} = \frac{1}{\sqrt{2}}(|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2) \times \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 + |\downarrow\rangle_1|\uparrow\rangle_2) \quad (S = 1, m_S = 0)$$

$$|\psi\rangle_{+} = \frac{1}{\sqrt{2}}(|a\rangle_1|b\rangle_2 + |b\rangle_1|a\rangle_2) \times \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2) \quad (S = 0, m_S = 0)$$

Thus the states $|\psi\rangle_{+}$ and $|\psi\rangle_{-}$ are also eigenstates of the total spin S

Two-electron systems (6)

- In summary, for two identical spin-half particles in *different* spatial states, the overall wavefunctions can be written in terms of eigenstates of total spin S as :

$S = 1 \text{ triplet}$

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2) \times \begin{cases} |\uparrow\rangle_1|\uparrow\rangle_2 \\ \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 + |\downarrow\rangle_1|\uparrow\rangle_2) \\ |\downarrow\rangle_1|\downarrow\rangle_2 \end{cases}$$

(*antisymmetric*)

(*symmetric*)

$S = 0 \text{ singlet}$

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|a\rangle_1|b\rangle_2 + |b\rangle_1|a\rangle_2) \times \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2)$$

(*symmetric*)

(*antisymmetric*)

Beyond 2-electron systems

- A similar factorisation into spatial and spin states of definite symmetry is also possible for a system consisting of two identical *bosons*

However, for systems containing *three or more* identical particles (fermions or bosons), the overall states do *not* in general factorise into separate spatial and spin components

- For an N -particle system with N large ($N \gg 1$), it is much easier (nay essential) to employ the techniques of *statistical physics* ...

(see the parallel Part II course on Thermal and Statistical Physics)

This allows the *probability distribution* for the single-particle state occupancies to be obtained (for a system in thermal equilibrium)

(the *Fermi-Dirac distribution* for identical fermions, and the *Bose-Einstein distribution* for identical bosons)

Exchange Forces

- Consider two *non-interacting* particles moving in one dimension, with each particle occupying distinct, orthonormal spatial states $|a\rangle$ and $|b\rangle$:

$$|a\rangle = \psi_a(x) ; \quad |b\rangle = \psi_b(x) ; \quad \langle a|b\rangle = 0$$

- For *distinguishable* particles, each particle unambiguously occupies a particular spatial state, giving two possible two-particle states :

$$\psi(x_1, x_2) = \begin{cases} \psi_a(x_1)\psi_b(x_2) \equiv |1, a\rangle|2, b\rangle \\ \psi_b(x_1)\psi_a(x_2) \equiv |1, b\rangle|2, a\rangle \end{cases}$$

- For *identical* particles, the spatial component of the two-particle state must be either symmetric or antisymmetric under particle interchange $1 \leftrightarrow 2$ (as on slides 6.15 or 6.21) :

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2))$$

$$|\psi\rangle = \frac{1}{\sqrt{2}} (|1, a\rangle|2, b\rangle \pm |1, b\rangle|2, a\rangle)$$

(6.23.1)

Exchange forces (2)

- The mean-square separation of the two particles is given by

$$\begin{aligned}\langle x_{12}^2 \rangle &\equiv \iint (x_1 - x_2)^2 |\psi(x_1, x_2)|^2 dx_1 dx_2 \\ &= \langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle\end{aligned}$$

- For *distinguishable* particles in the state $|1,a\rangle|2,b\rangle$, we have

$$\begin{aligned}\langle x_1^2 \rangle &= \langle 1, a | x_1^2 | 1, a \rangle \langle 2, b | 2, b \rangle = \langle x^2 \rangle_a \\ \langle x_2^2 \rangle &= \langle 1, a | 1, a \rangle \langle 2, b | x_2^2 | 2, b \rangle = \langle x^2 \rangle_b \\ \langle x_1 x_2 \rangle &= \langle 1, a | x_1 | 1, a \rangle \langle 2, b | x_2 | 2, b \rangle = \langle x \rangle_a \langle x \rangle_b\end{aligned}$$

where, for example :

$$\langle x^2 \rangle_a = \int x^2 |\psi_a(x)|^2 dx$$

Hence

$$\langle x_{12}^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$$

- The same expression is obtained also for the state $|1,b\rangle|2,a\rangle$

Exchange forces (3)

- For *identical* particles, the spatial component of the two-particle state is as in equation (6.23.1) :

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|1, a\rangle|2, b\rangle \pm |1, b\rangle|2, a\rangle)$$

We now have

$$\begin{aligned}\langle x_1^2 \rangle &= \frac{1}{2} \langle 1, a | x_1^2 | 1, a \rangle \langle 2, b | 2, b \rangle + \frac{1}{2} \langle 1, b | x_1^2 | 1, b \rangle \langle 2, a | 2, a \rangle \\ &\quad \pm \frac{1}{2} \langle 1, a | x_1^2 | 1, b \rangle \langle 2, b | 2, a \rangle \pm \frac{1}{2} \langle 1, b | x_1^2 | 1, a \rangle \langle 2, a | 2, b \rangle\end{aligned}$$

- Orthonormality of the spatial states $|a\rangle$ and $|b\rangle$ then gives

$$\langle x_1^2 \rangle = \frac{1}{2} \langle x^2 \rangle_a + \frac{1}{2} \langle x^2 \rangle_b \quad \left\{ \begin{array}{l} \langle a | a \rangle = \langle b | b \rangle = 1 \\ \langle a | b \rangle = 0 \end{array} \right.$$

Similarly (just interchange a and b) :

$$\langle x_2^2 \rangle = \frac{1}{2} \langle x^2 \rangle_b + \frac{1}{2} \langle x^2 \rangle_a$$

Exchange forces (4)

- We also have (for identical particles)

$$\begin{aligned}\langle x_1 x_2 \rangle &= \frac{1}{2} \langle 1, a | x_1 | 1, a \rangle \langle 2, b | x_2 | 2, b \rangle + \frac{1}{2} \langle 1, b | x_1 | 1, b \rangle \langle 2, a | x_2 | 2, a \rangle \\ &\pm \frac{1}{2} \langle 1, a | x_1 | 1, b \rangle \langle 2, b | x_2 | 2, a \rangle \pm \frac{1}{2} \langle 1, b | x_1 | 1, a \rangle \langle 2, a | x_2 | 2, b \rangle\end{aligned}$$

- This is

$$\langle x_1 x_2 \rangle = \frac{1}{2} \langle x \rangle_a \langle x \rangle_b + \frac{1}{2} \langle x \rangle_a \langle x \rangle_b \pm \frac{1}{2} x_{ab} x_{ba} \pm \frac{1}{2} x_{ab} x_{ba}$$

where

$$x_{ab} \equiv \langle a | x | b \rangle = \int \psi_a^*(x) x \psi_b(x) dx = x_{ba}^* \quad (6.26.1)$$

$$\Rightarrow \quad \langle x_1 x_2 \rangle = \langle x \rangle_a \langle x \rangle_b \pm |x_{ab}|^2$$

- The mean-square separation of the two identical particles is therefore

$$\begin{aligned}\langle x_{12}^2 \rangle &= \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle \\ &= \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |x_{ab}|^2\end{aligned}$$

Exchange forces (5)

- In summary, for two non-interacting particles occupying distinct spatial states, the mean square separation is

$$\langle x_{12}^2 \rangle = \begin{cases} \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b & \text{distinguishable} \\ \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b - 2|x_{ab}|^2 & \text{symmetric} \\ \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b + 2|x_{ab}|^2 & \text{antisymmetric} \end{cases}$$

Hence, even if the particles are non-interacting :

identical particles are closer together, or further apart, on average than distinguishable particles occupying the same spatial states

- As specific examples :
 - two identical spin-zero particles are closer together on average than two distinguishable particles occupying the same pair of states
 - two identical spin-half particles in a spin-singlet (spin-triplet) state are closer together (further apart) on average than distinguishable particles in the same pair of spatial states

Exchange forces (6)

- A particular realisation of the above results (for a one-dimensional system), can be found on the Examples Sheet

(optional extra: verify explicitly the formulae on the previous slide for the example given)

- The quantity responsible for the differences in mean-square separation is x_{ab} , as defined in equation (6.26.1) :

$$x_{ab} \equiv \int \psi_a^*(x) x \psi_b(x) dx$$

This quantity vanishes if $\psi_a(x)$ and $\psi_b(x)$ do not overlap

→ identical particles very far apart are *effectively* distinguishable

- If the wavefunctions do overlap, identical particles behave *effectively* as if there is an *exchange force* of repulsion (attraction) between them when they are in an antisymmetric (symmetric) spatial state

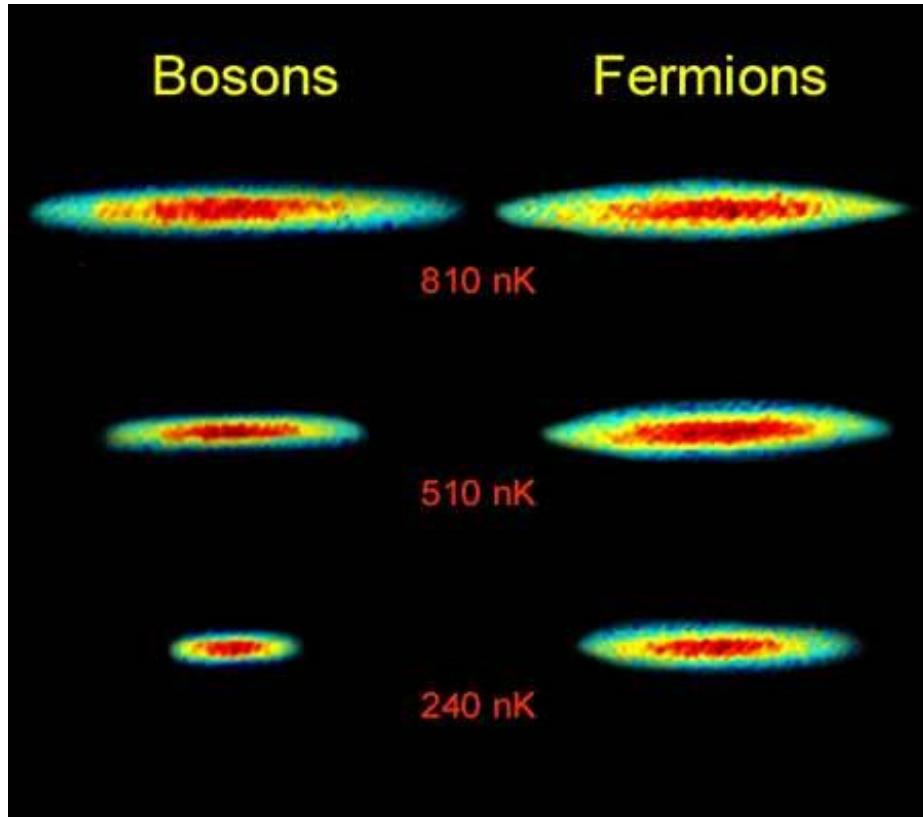
This is a strictly quantum mechanical effect, with no classical analogue

- The above is all for $N = 2$; for $N \gg 1$ see the PtII TSP course
 - degeneracy pressure, Bose-Einstein condensation, ...

Bosons vs Fermions

- The difference between bosons and fermions has been nicely demonstrated within a single experiment :

[A. G. Truscott et al., Science 291 \(2001\) 2570](#)



${}^7\text{Li}$

($F = 2, m_F = 2$)

($Z = 3$)

${}^6\text{Li}$

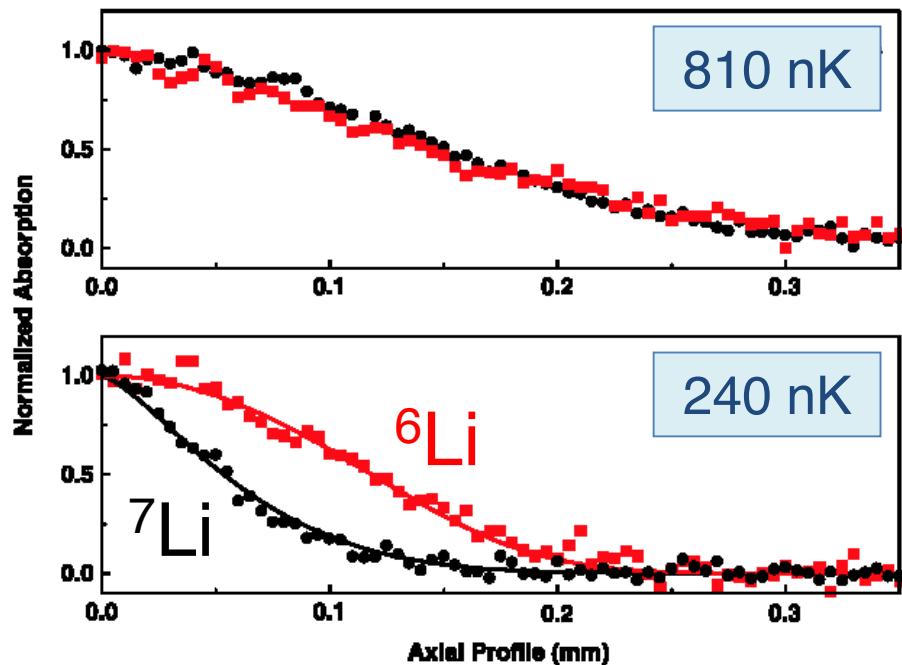
($F = 3/2$)

Cooling fermions is difficult :
standard “evaporative cooling”
techniques cannot be applied

Achieved in this experiment by
simultaneously cooling fermions
(${}^6\text{Li}$ atoms) and bosons (${}^7\text{Li}$ atoms)

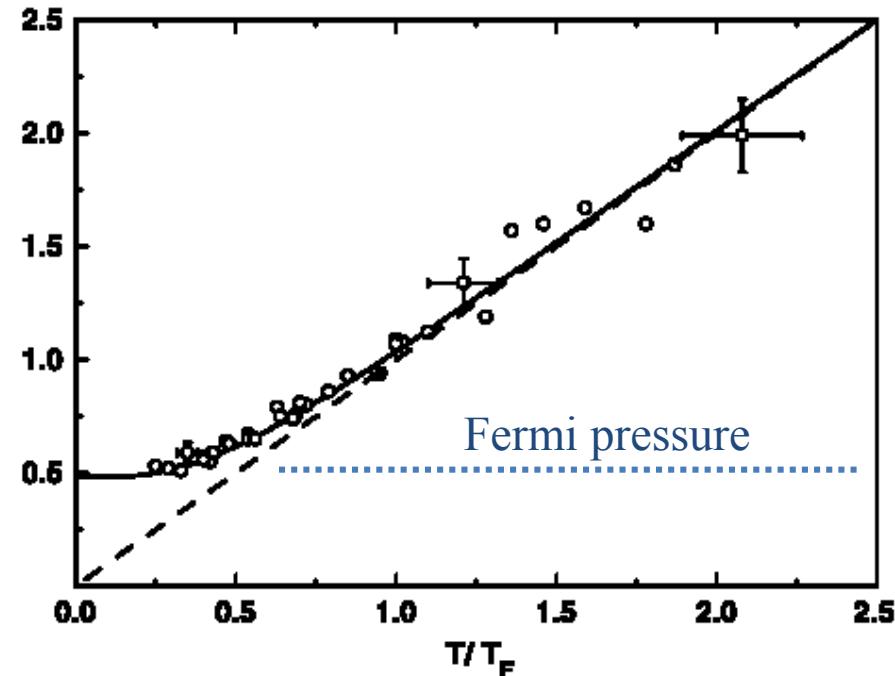
The atoms are optically pumped into
hyperfine states $|F, m_F\rangle$ which are
suitable for magnetic trapping

Bosons vs Fermions (2)



Axial profiles of atoms
within the trap

Axial squared radius vs
temperature for ^{6}Li cloud



solid line : prediction for ideal
Fermi gas

dashed line : prediction from
classical statistics

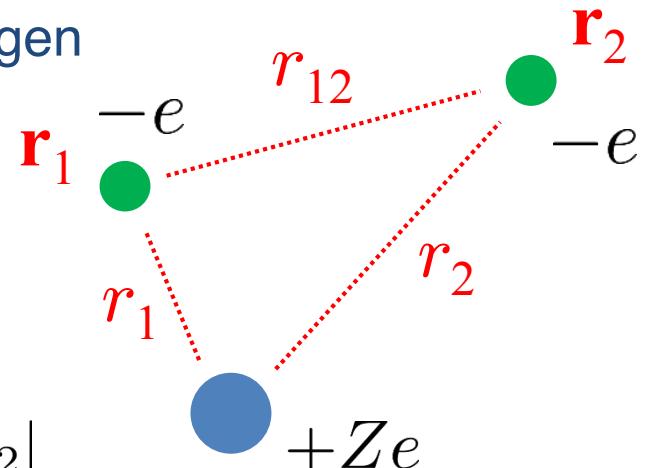
(Fermi pressure is responsible for
holding up white dwarf and neutron
stars against gravitational collapse)

The Helium Atom

- Helium ($Z = 2$) is the simplest atom after hydrogen

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}} \right)$$

$$r_{12} \equiv |\mathbf{r}_1 - \mathbf{r}_2|$$



(assuming an infinite mass nucleus, non-relativistic electrons, neglecting spin-orbit and spin-spin interactions, ...)

- The Schrödinger equation for helium is analytically intractable because of the electron-electron Coulomb interaction proportional to $1/r_{12}$
 - we first switch it off (“zeroth-order helium”)
 - we then use the *variational method* to estimate its effect

The “Zeroth-Order” Helium Atom

- Neglecting the electron-electron Coulomb interaction gives the Hamiltonian for the helium atom as

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \quad (Z = 2)$$

This is the sum of two independent hydrogen-like Hamiltonians :

$$\hat{H} = \hat{H}_1 + \hat{H}_2 ; \quad \hat{H}_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i}$$

- Neglecting electron spin, the eigenstates of H are therefore the product of two hydrogen-like eigenstates :

$$\hat{H} [|n_1\ell_1m_1\rangle |n_2\ell_2m_2\rangle] = (E_1 + E_2) [|n_1\ell_1m_1\rangle |n_2\ell_2m_2\rangle]$$

$$E_1 + E_2 = - \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) Z^2 R_\infty$$

Zeroth-order helium : the ground state

- The ground state (of energy E_0) is obtained by taking the two principal quantum numbers to be $n_1 = n_2 = 1$

The spatial component of the ground state wavefunction is therefore

$$|\psi\rangle = |100\rangle|100\rangle ; \quad E_0 = -2Z^2R_\infty = -8R_\infty$$

which is *symmetric* under interchange $1 \leftrightarrow 2$

- The two electrons are identical fermions; the ground state wavefunction must therefore be antisymmetric overall, with an antisymmetric spin component :

$$|\psi\rangle = \frac{1}{\sqrt{2}} [|100\uparrow\rangle|100\downarrow\rangle - |100\downarrow\rangle|100\uparrow\rangle]$$

$$|\psi\rangle = |100\rangle|100\rangle \times \frac{1}{\sqrt{2}} [|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle]$$

Thus the ground state of the helium atom is non-degenerate ($g = 1$), and must have total spin $S = 0$

Zeroth-order helium : excited states

- Consider excited states of helium with one electron in the 1s ground state ($n_1 = 1$ or $n_2 = 1$) and the other electron in an excited hydrogen-like state :

$$|100\rangle|n\ell m\rangle ; \quad |n\ell m\rangle|100\rangle$$

- Taking electron spin into account, such *single-particle* excited states can have either total spin $S = 0$ (*parahelium*)

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|100\rangle|n\ell m\rangle + |n\ell m\rangle|100\rangle) \times \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

or total spin $S = 1$ (*orthohelium*)

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|100\rangle|n\ell m\rangle - |n\ell m\rangle|100\rangle) \times \begin{cases} |\uparrow\rangle|\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle) \\ |\downarrow\rangle|\downarrow\rangle \end{cases}$$

- The single-particle excited state of lowest energy, E_1 , is obtained by taking $n_1 = 1, n_2 = 2$ or $n_1 = 2, n_2 = 1$:

$$|100\rangle|2\ell m\rangle \quad \text{or} \quad |2\ell m\rangle|100\rangle ; \quad E_1 = -\frac{5}{4}Z^2R_\infty = -5R_\infty$$

Zeroth-order helium : two-particle excited states

- Now consider *two-particle* excited states, where *both* electrons are excited out of the 1s ground state :

$$|n_1\ell_1m_1\rangle|n_2\ell_2m_2\rangle \quad (n_1 \geq 2, n_2 \geq 2)$$

The lowest energy two-particle excited states, of energy E_2 , would be obtained by taking $n_1 = n_2 = 2$:

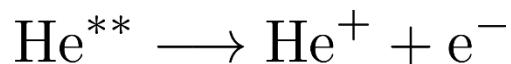
$$|2\ell_1m_1\rangle|2\ell_2m_2\rangle ; \quad E_2 = -\frac{1}{2}Z^2R_\infty = -2R_\infty$$

- However, at zeroth-order, such two-particle excited states cannot exist :
The He^+ ion is a hydrogen-like atom with $Z = 2$, and so has ground state energy

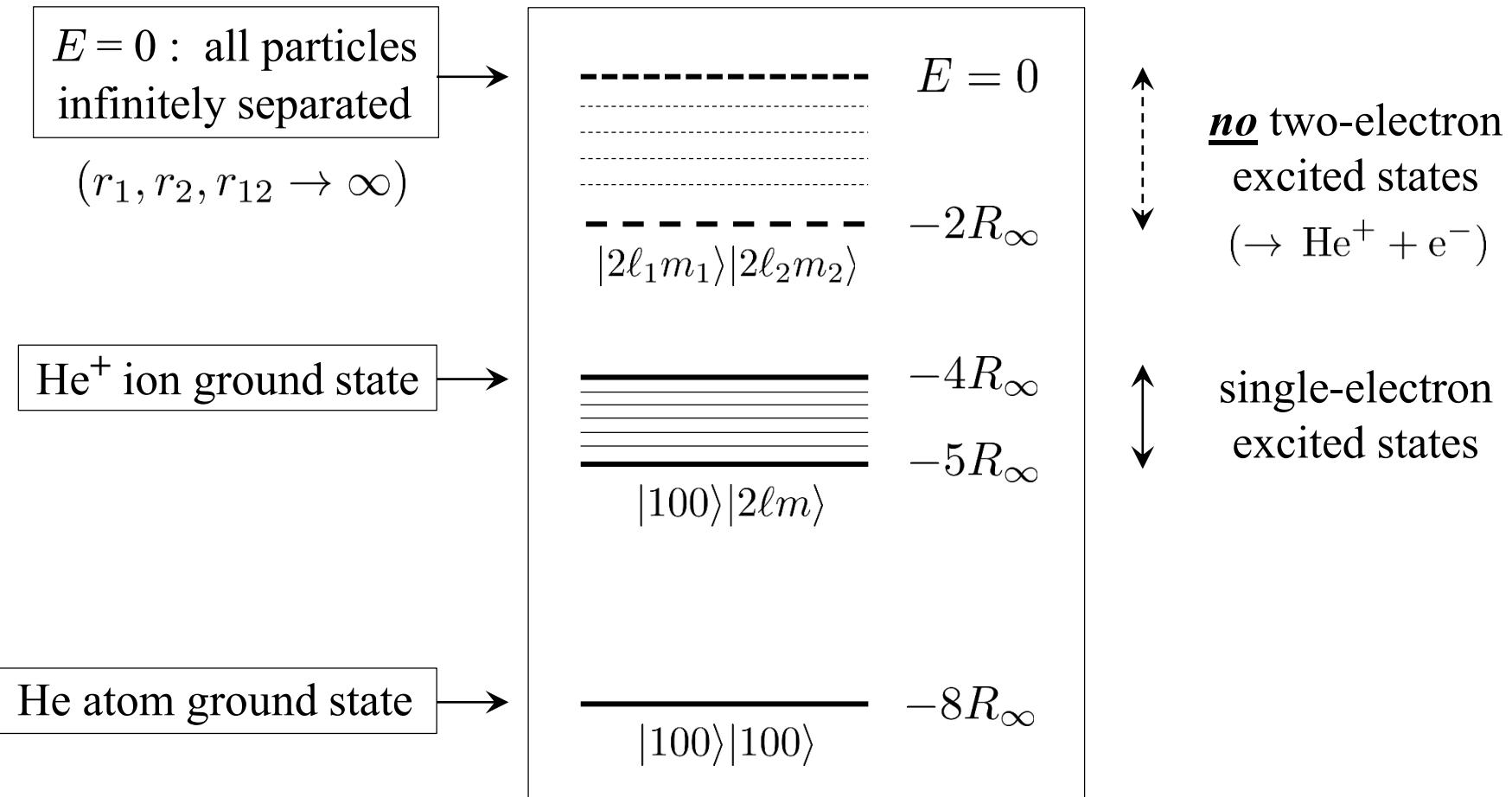
$$E_0(\text{He}^+) = -Z^2R_\infty = -4R_\infty$$

This is *below* the energy ($E_2 = -2R_\infty$) of the lowest possible two-particle excited state of the helium atom

→ a two-particle excited state He^{**} would rapidly auto-ionise as



Zeroth-order helium : two-particle excited states (2)



- This is all at zeroth-order, but the conclusion remains essentially the same when Coulomb repulsion is included
(of 198 levels listed in the [NIST database](#), only 4 are two-particle excited states)

Zeroth-order helium : excited states

- In summary, helium atom states are almost all of the form $|100\rangle|n\ell m\rangle$, where the possible states $|n\ell m\rangle$ are the same as for hydrogen :

n	ℓ	subshells
1	0	1s
2	0, 1	2s, 2p
3	0, 1, 2	3s, 3p, 3d
4	0, 1, 2, 3	4s, 4p, 4d, 4f
...
n	$0, 1, 2, 3, \dots, (n - 1)$	ns, np, ...

- The state $|100\rangle|n\ell m\rangle$ has angular momentum quantum numbers given by

$$\hat{\mathbf{L}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2 ; \quad \hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 ; \quad \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

$$\ell_1 = 0, \quad \ell_2 = 0, 1, 2, \dots, (n - 1) \quad \Rightarrow \quad L = 0, 1, 2, \dots, (n - 1)$$

$$s_1 = 1/2, \quad s_2 = 1/2 \quad \Rightarrow \quad S = 0, 1$$

$$J = L \quad (\text{if } S = 0) ; \quad J = L, L \pm 1 \quad (\text{if } S = 1)$$

Zeroth-order helium : summary of eigenstates

subshells $(n_1\ell_1)(n_2\ell_2)$	ℓ_1	ℓ_2	L	parahelium $(S = 0)$	orthohelium $(S = 1)$
(1s)(1s)	0	0	0	$J = 0$ 1S_0	
(1s)(2s)	0	0	0	$J = 0$ 1S_0	$J = 1$ 3S_1
(1s)(2p)	0	1	1	$J = 1$ 1P_1	$J = 0, 1, 2$ $^3P_{0,1,2}$
(1s)(3d)	0	2	2	$J = 2$ 1D_2	$J = 1, 2, 3$ $^3D_{1,2,3}$
(1s)(4f)	0	3	3	$J = 3$ 1F_3	$J = 2, 3, 4$ $^3F_{2,3,4}$

$L = \ell_1 \otimes \ell_2$ $J = L \otimes S$ $(2S+1)L_J$

- The ground state (the first row) can have $S = 0$ only (slide 6.34)
- The energies of the zeroth-order states depend only on n_1, n_2 :

$$E = - \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) Z^2 R_\infty$$

i.e. the energies are independent of L, m_L, S, m_S, J, m_J

→ at zeroth-order, all excited states of helium are degenerate

Ground State Energy of Helium

Now “switch on” the $1/r_{12}$ Coulomb repulsion between the two electrons :

- The Hamiltonian for the helium atom can be separated as

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) ; \quad \hat{H}' = \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

- H_0 is the sum of two independent hydrogen atom Hamiltonians, with (known) ground state wavefunction (slide 6.34)

$$\begin{aligned} |\psi_0\rangle &= |100(\mathbf{r}_1)\rangle|100(\mathbf{r}_2)\rangle \times \frac{1}{\sqrt{2}} [|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle] \\ &= \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0} \times \frac{1}{\sqrt{2}} [|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle] \end{aligned} \tag{6.40.1}$$

The ground state energy is $E_0 = -2Z^2R_\infty = -8R_\infty$

Ground state energy of helium (2)

- It is tempting to treat the e-e Coulomb interaction H' as a perturbation
However H' is not small relative to the other terms in H
→ no reason *a priori* to expect perturbation theory to be successful
Instead, we apply the *variational method* to the complete Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}} \right)$$

- As the trial wavefunction, we maintain the *form* of the wavefunction in equation (6.40.1), but treat Z as a variational parameter (Z') :

$$|\psi_{\text{trial}}(Z')\rangle = \frac{(Z')^3}{\pi a_0^3} e^{-Z'(r_1+r_2)/a_0}$$

The parameter Z' can be regarded as taking into account the *screening* of the positive nuclear charge by the other electron

→ we expect to find $1 < Z' < 2$ (for $Z = 2$)

Ground state energy of helium (3)

- The variational method requires us to minimise the expectation value

$$E(Z') = \langle \psi(Z') | \hat{H} | \psi(Z') \rangle = E_1 + E_2 + E_{12}$$

where

$$E_1 \equiv \left\langle \psi(Z') \left| -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \right| \psi(Z') \right\rangle$$

$$E_2 \equiv \left\langle \psi(Z') \left| -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \right| \psi(Z') \right\rangle$$

$$E_{12} \equiv \frac{e^2}{4\pi\epsilon_0} \left\langle \psi(Z') \left| \frac{1}{r_{12}} \right| \psi(Z') \right\rangle$$

- The trial wavefunction is the product of two hydrogen-like wavefunctions :

$$|\psi(Z')\rangle = |\psi'_{100}(\mathbf{r}_1)\rangle |\psi'_{100}(\mathbf{r}_2)\rangle$$

Hence the E_1 and E_2 contributions are given by

$$E_1 = E_2 = \left\langle \psi'_{100}(\mathbf{r}) \left| -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right| \psi'_{100}(\mathbf{r}) \right\rangle$$

Ground state energy of helium (4)

- Writing the hydrogen-like wavefunctions as

$$|\psi'_{100}(\mathbf{r})\rangle = \sqrt{\frac{(Z')^3}{\pi a_0^3}} e^{-Z'r/a_0} \equiv \sqrt{\frac{\beta^3}{\pi}} e^{-\beta r} ; \quad \beta \equiv \frac{Z'}{a_0}$$

we have

$$\langle \psi' | \nabla^2 | \psi' \rangle = \frac{\beta^3}{\pi} \int e^{-\beta r} (\nabla^2 e^{-\beta r}) d^3 \mathbf{r} = 4\beta^3 \int_0^\infty r^2 e^{-\beta r} (\nabla^2 e^{-\beta r}) dr$$

$$\langle \psi' | \frac{1}{r} | \psi' \rangle = \frac{\beta^3}{\pi} \int \frac{1}{r} e^{-2\beta r} d^3 \mathbf{r} = 4\beta^3 \int_0^\infty r e^{-2\beta r} dr$$

- These integrals were calculated earlier (slide 2.48) :

$$\langle \psi' | \frac{1}{r} | \psi' \rangle = \beta ; \quad \langle \psi' | \nabla^2 | \psi' \rangle = -\beta^2$$

Hence the E_1 and E_2 contributions are

$$E_1 = E_2 = ((Z')^2 - 2ZZ') R_\infty$$

(6.43.1)

Ground state energy of helium (5)

- The E_{12} contribution is

$$E_{12} = \frac{e^2}{4\pi\epsilon_0} \left(\frac{(Z')^3}{\pi a_0^3} \right)^2 \iint \frac{e^{-2Z'(r_1+r_2)/a_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

Using the standard integral (derived in Appendix A, for completeness)

$$\iint \frac{e^{-(r_1+r_2)/r_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 20\pi^2 r_0^5$$

the E_{12} contribution is obtained as

$$(r_0 = a_0/2Z')$$

$$E_{12} = \frac{e^2}{4\pi\epsilon_0} \left(\frac{(Z')^3}{\pi a_0^3} \right)^2 (20\pi^2) \left(\frac{a_0}{2Z'} \right)^5$$

- This tidies up as

$$E_{12} \equiv \frac{e^2}{4\pi\epsilon_0} \langle \psi(Z') | \frac{1}{r_{12}} | \psi(Z') \rangle = \frac{5}{4} Z' R_\infty$$

(6.44.1)

Ground state energy of helium (6)

- Summing equations (6.43.1) and (6.44.1), the total energy $E(Z')$ is therefore

$$E(Z') = E_1 + E_2 + E_{12} = \left(2(Z')^2 - 4ZZ' + \frac{5}{4}Z' \right) R_\infty \quad (6.45.1)$$

Minimising with respect to Z' gives

$$0 = \frac{\partial E(Z')}{\partial Z'} = \left(4Z' - 4Z + \frac{5}{4} \right) R_\infty \quad \Rightarrow \quad \boxed{Z' = Z - \frac{5}{16}}$$

- Substituting this value of Z' into equation (6.45.1) then gives an upper bound on the ground state energy :

$$\boxed{E(Z') = -2(Z')^2 R_\infty = -2 \left(Z - \frac{5}{16} \right)^2 R_\infty} \quad (6.45.2)$$

Ground state energy of helium (7)

- For helium ($Z = 2$), this gives $Z' = 27/16$ (i.e. $1 < Z' < 2$, as expected)

The estimate of the helium ground state energy from the variational method is then

$$E(Z') = E(27/16) = -2 \left(\frac{27}{16} \right)^2 R_\infty \approx -(5.695)R_\infty \approx \boxed{-77.4 \text{ eV}}$$

This is only about $(0.12)R_\infty$ (≈ 1.6 eV) above the measured value :

$$(E_0)_{\text{meas}} \approx -(5.81)R_\infty \approx \boxed{-79.0 \text{ eV}}$$

“.. within 2% of the correct answer, and, frankly, at this point, my own interest in the problem begins to wane.”

(D. Griffiths & D. Schroeter, “Quantum Mechanics”, 3rd edn., CUP, 2018; p336)

- The variational estimate is well above the zeroth-order ground state energy :

$$E_0^{(0)} = -8R_\infty \approx -109 \text{ eV}$$

→ the $1/r_{12}$ Coulomb repulsion is indeed not a small effect

Helium atom ground state : perturbation theory

- Were we to use *perturbation theory* in place of the variational method, the first-order energy correction would be given as

$$\Delta E_0^{(1)} = \langle \psi_0 | \hat{H}' | \psi_0 \rangle ; \quad \hat{H}' = \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where $|\psi_0\rangle$ is the zeroth-order helium ground state of equation (6.40.1)

- This involves the same calculation as already carried out for E_{12} above, with Z in place of Z' ; equation (6.44.1) immediately gives

$$\Delta E_0^{(1)} = E_{12}(Z) = \frac{5}{4} Z R_\infty$$

- Hence perturbation theory gives a first-order helium atom ground state energy

$$E_0 = \left(-2Z^2 + \frac{5}{4}Z \right) R_\infty = -\frac{11}{2} R_\infty = \boxed{-74.7 \text{ eV}}$$

→ not as good an estimate as the variational method, but much better than might *a priori* have been expected

Helium atom : ionisation energy

- It is convenient to convert the (negative) helium ground state energy, $E_0 < 0$, into a (positive) ionisation energy, $J > 0$:

The ionisation energy, J , is defined as the energy required to remove one of the electrons from the helium atom, leaving behind an He^+ ion :

$$J \equiv E_0(\text{He}^+) - E_0(\text{He}) > 0$$

(see slide 6.37)

- Ionisation of a two-electron atom or ion leaves behind a system consisting of a single electron orbiting a nucleus of charge Ze

This hydrogen-like system has ground state energy $-Z^2 R_\infty$; hence the ionisation energy, J_1 , predicted by the one-parameter variational method is

$$J_1 = \left[-Z^2 + 2 \left(Z - \frac{5}{16} \right)^2 \right] R_\infty$$

(6.48.1)

- For helium ($Z=2$), the prediction is about 6% below the right answer :

$$J_1 = (1.695)R_\infty = 23.1 \text{ eV} \quad (J_{\text{meas}} = 24.6 \text{ eV})$$

The hydrogen ion H^-

- For the negative hydrogen ion, H^- ($Z = 1$), equation (6.48.1) gives a *negative* ionisation energy

$$J_1(H^-) \approx -(0.055)R_\infty \approx -0.75 \text{ eV}$$

i.e. it predicts that no H^- bound state exists

- However the H^- ion definitely *does* exist !

$$J_{\text{meas}}(H^-) \approx +(0.055)R_\infty \approx +0.75 \text{ eV}$$

(albeit possessing only a ground state; H^- has no excited states)

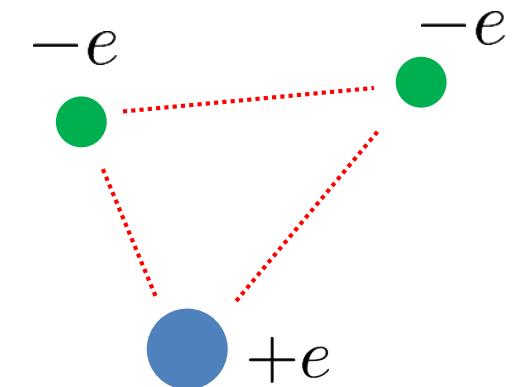
- At CERN, a new linac which accelerates H^- ions has recently been commissioned as the first stage of the CERN LHC accelerator chain

[Linac-4 press release](#)

The H^- ions are converted to protons in subsequent stages of the chain

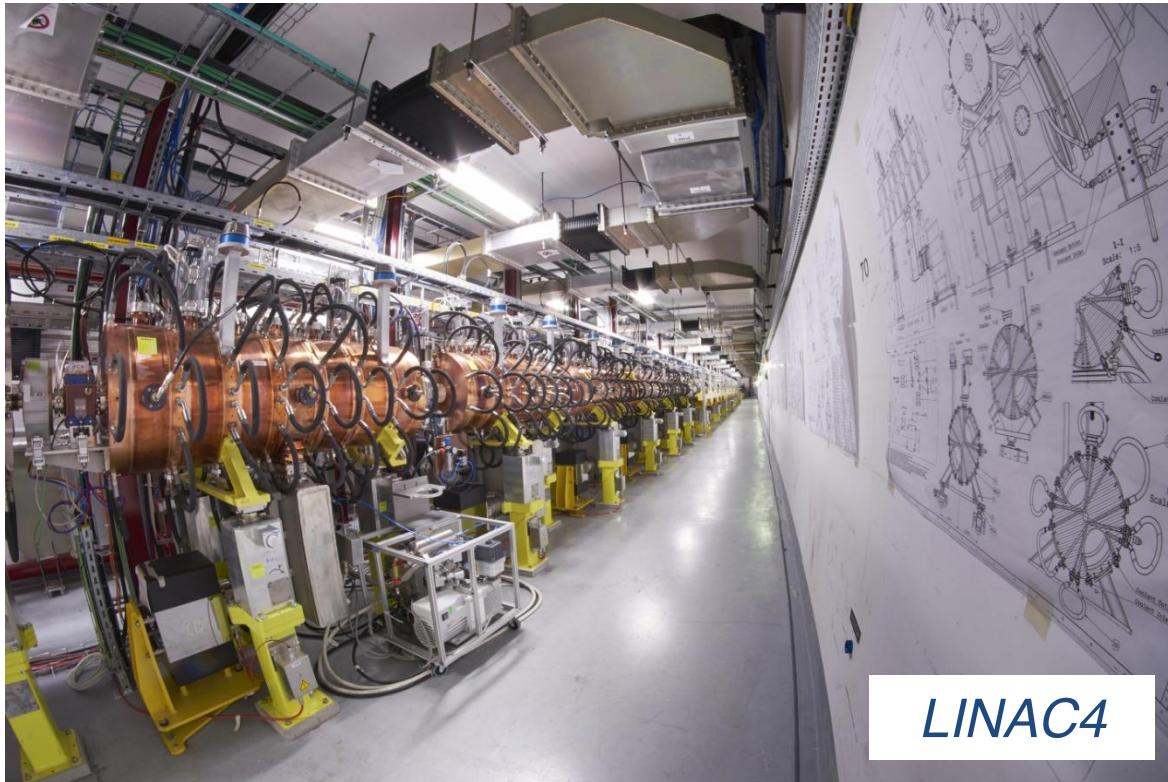
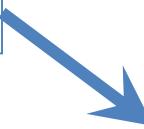
(starting with H^- ions rather than protons has accelerator-physics advantages which allows the final proton beam intensity to be more than doubled)

- The H^- ion is also the main source of opacity in the solar atmosphere



The hydrogen ion H^-

The source of all protons at CERN



<https://home.cern/science/accelerators/linear-accelerator-4>



- Since H^- definitely exists, we clearly need to improve on the one-parameter variational calculation considered so far ...

Helium : improved variational estimates

- To obtain improved predictions, we can add more variational parameters (i.e. go beyond the single variational parameter, Z')

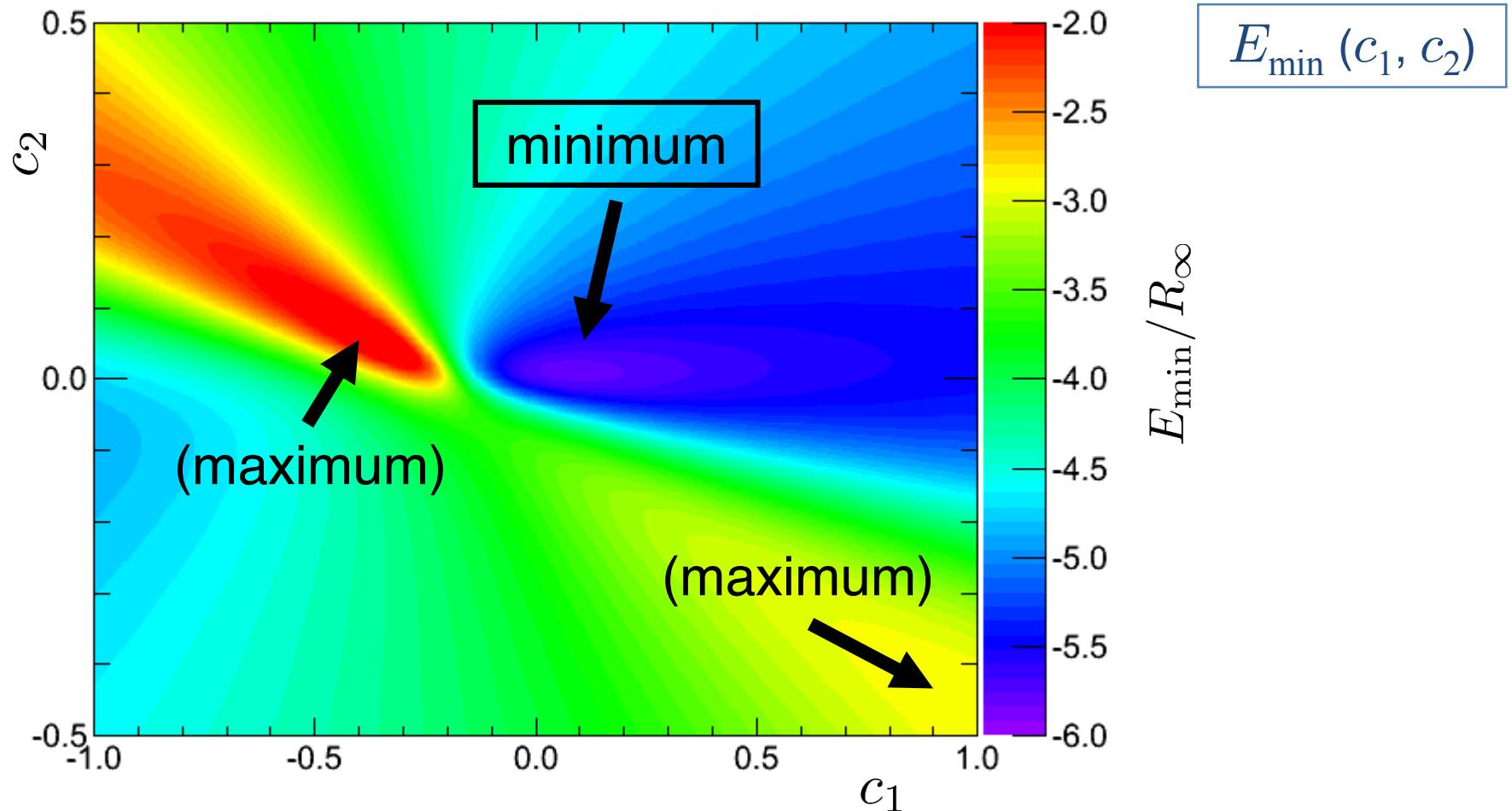
For example, use three parameters, k, c_1, c_2 , with a trial wavefunction of the Hylleraas form :

$$\psi(s, t, u) = e^{-ks/2} (1 + c_1 k u + c_2 k^2 t^2)$$
$$s \equiv r_1 + r_2 , \quad t \equiv r_1 - r_2 , \quad u \equiv r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$$

This choice of trial wavefunction maintains spatial symmetry under the interchange $1 \leftrightarrow 2$ of the two (identical) electrons

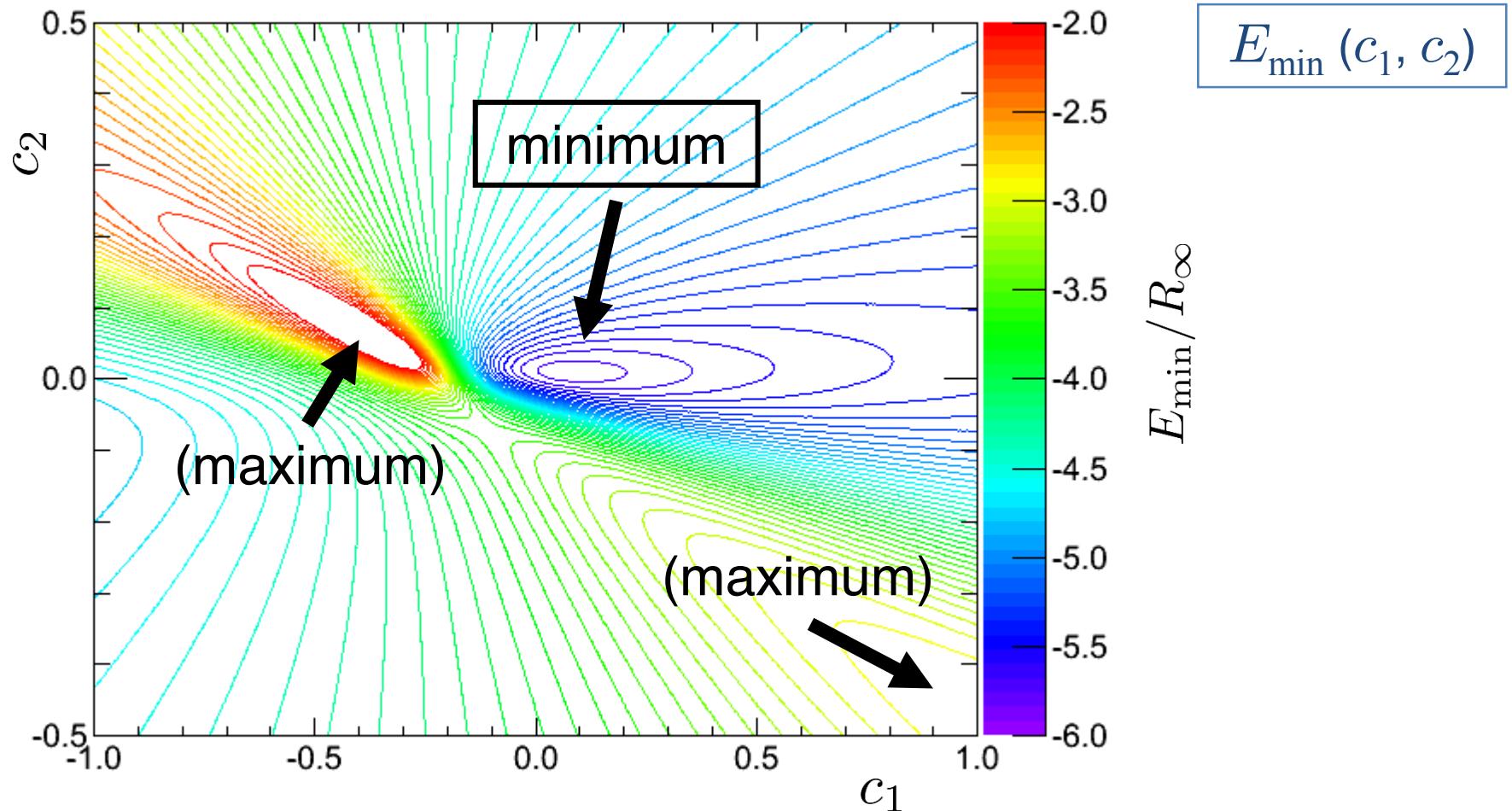
- The minimisation is easiest carried out as a two-step process :
 - 1) Minimise $E(k, c_1, c_2)$ with respect to k , for given values of (c_1, c_2)
→ $E_{\min}(c_1, c_2)$ (this step can be carried out analytically)
 - 2) Search for the overall minimum of $E_{\min}(c_1, c_2)$ in the (c_1, c_2) plane
(this step can only be carried out numerically ... see the plot below)

Helium : improved variational estimates (2)



- The overall minimum is found at $(c_1, c_2, k) = (0.081, 0.010, 3.63)$, with
$$E_{\min} = -(5.80488)R_\infty$$

Helium : improved variational estimates (2)



- The overall minimum is found at $(c_1, c_2, k) = (0.081, 0.010, 3.63)$, with
$$E_{\min} = -(5.80488)R_\infty$$

Helium : improved variational estimates (3)

- Using three parameters gives a much improved prediction (within 0.2%) for the ground state ionisation energy of the helium atom :

$$J_3(\text{He}) = (-4R_\infty) - (-5.80488R_\infty) \approx 1.80488 R_\infty \quad (J_{\text{meas}} = 1.80714 R_\infty)$$

Furthermore, the 3-parameter minimisation also correctly predicts that the H^- ion really does exist (i.e. it predicts $J > 0$) :

$$J_3(\text{H}^-) = +0.0506 R_\infty \quad (J_{\text{meas}} = +0.055 R_\infty)$$

- The current state of the art uses trial wavefunctions containing up to about 24000 terms to obtain the non-relativistic energies and wavefunctions

The non-relativistic ground state energy of the helium atom is known to 46 significant digits

[C. Schwartz, arXiv:math-ph/0605018 \(2006\)](https://arxiv.org/abs/math-ph/0605018)

The H^- ion is known to 34 significant digits

[D. Aznabaev, A. Bekbaev & V. Korobov, Phys. Rev. A 98 \(2018\) 012510](https://doi.org/10.1103/PhysRevA.98.012510)

These can then be used as the starting point for calculations which also include nuclear recoil effects, relativistic corrections, QED corrections etc.

Helium : improved variational estimates (4)

- For the helium atom ground state, theory and experiment currently agree to better than one part in 10^8 :

$$J_{\text{QED}}(\text{He}) = 5\ 945\ 204\ 173(36) \text{ MHz}$$

$$J_{\text{meas}}(\text{He}) = 5\ 945\ 204\ 212(6) \text{ MHz}$$

[K. Pachucki, V. Patkos & A. Yerokhin, Phys. Rev. A 95 \(2017\) 062510](#)

[D. Kandula et al., Phys. Rev. A 84 \(2011\) 062512](#)

- In general (not just for helium), calculating atomic *energies* is only one consideration :
 - accurate *wavefunctions* are needed as inputs to many calculations (transition rates, polarisabilities, cross sections, ...)
 - these can benefit from using additional variational parameters, even if the energies have been well determined already
 - many atomic and ionic states (of relevance to astrophysics for example) cannot be studied in the lab – theoretical calculations are the only way
 - helium etc. form a testbed for such calculations

Excited States of Helium

- Now consider the effect of the electron-electron $1/r_{12}$ Coulomb interaction on the energies of *excited* states
 - we use perturbation theory rather than the variational method
- The unperturbed (zeroth-order) wavefunctions for excited states have a spatial component

$$|n\ell m^{(0)}\rangle = \frac{1}{\sqrt{2}}(|100(\mathbf{r}_1)\rangle|n\ell m(\mathbf{r}_2)\rangle \pm |n\ell m(\mathbf{r}_1)\rangle|100(\mathbf{r}_2)\rangle)$$

with “+” for $S = 0$ (parahelium), and “−” for $S = 1$ (orthohelium)

- The first-order energy correction is given by

$$\Delta E_{n\ell m}^{(1)} = \langle n\ell m^{(0)} | \hat{H}' | n\ell m^{(0)} \rangle ; \quad \hat{H}' = \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$\Delta E_{n\ell m}^{(1)} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \frac{|\psi_{100}(\mathbf{r}_1)\psi_{n\ell m}(\mathbf{r}_2) \pm \psi_{n\ell m}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

Excited states of helium (2)

- Since H' is a scalar operator, the matrix element must be independent of m (rotational symmetry, the Wigner-Eckart theorem) :

$$\Delta E_{n\ell m}^{(1)} = J_{n\ell} \pm K_{n\ell} \quad (6.57.1)$$

Choosing $m = 0$, we obtain

$$J_{n\ell} = \frac{e^2}{4\pi\epsilon_0} \int \frac{|\psi_{100}(\mathbf{r}_1)|^2 |\psi_{n\ell 0}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

$$K_{n\ell} = \frac{e^2}{4\pi\epsilon_0} \int \frac{\psi_{100}^*(\mathbf{r}_1) \psi_{n\ell 0}^*(\mathbf{r}_2) \psi_{100}(\mathbf{r}_2) \psi_{n\ell 0}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

- The $J_{n\ell}$ term represents the electrostatic interaction energy associated with two charge distributions, $|\psi_{100}(\mathbf{r})|^2$ and $|\psi_{n\ell 0}(\mathbf{r})|^2$, and we clearly have

$$J_{n\ell} > 0$$

This breaks the degeneracy in ℓ for each n

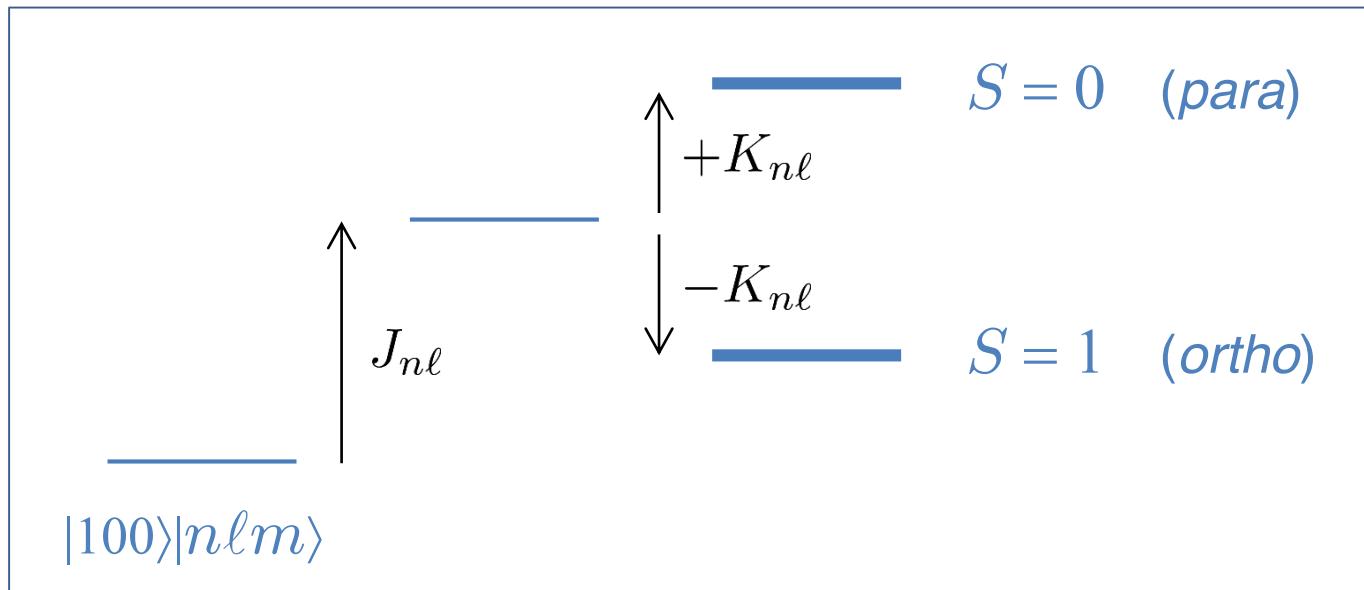
Excited states of helium (3)

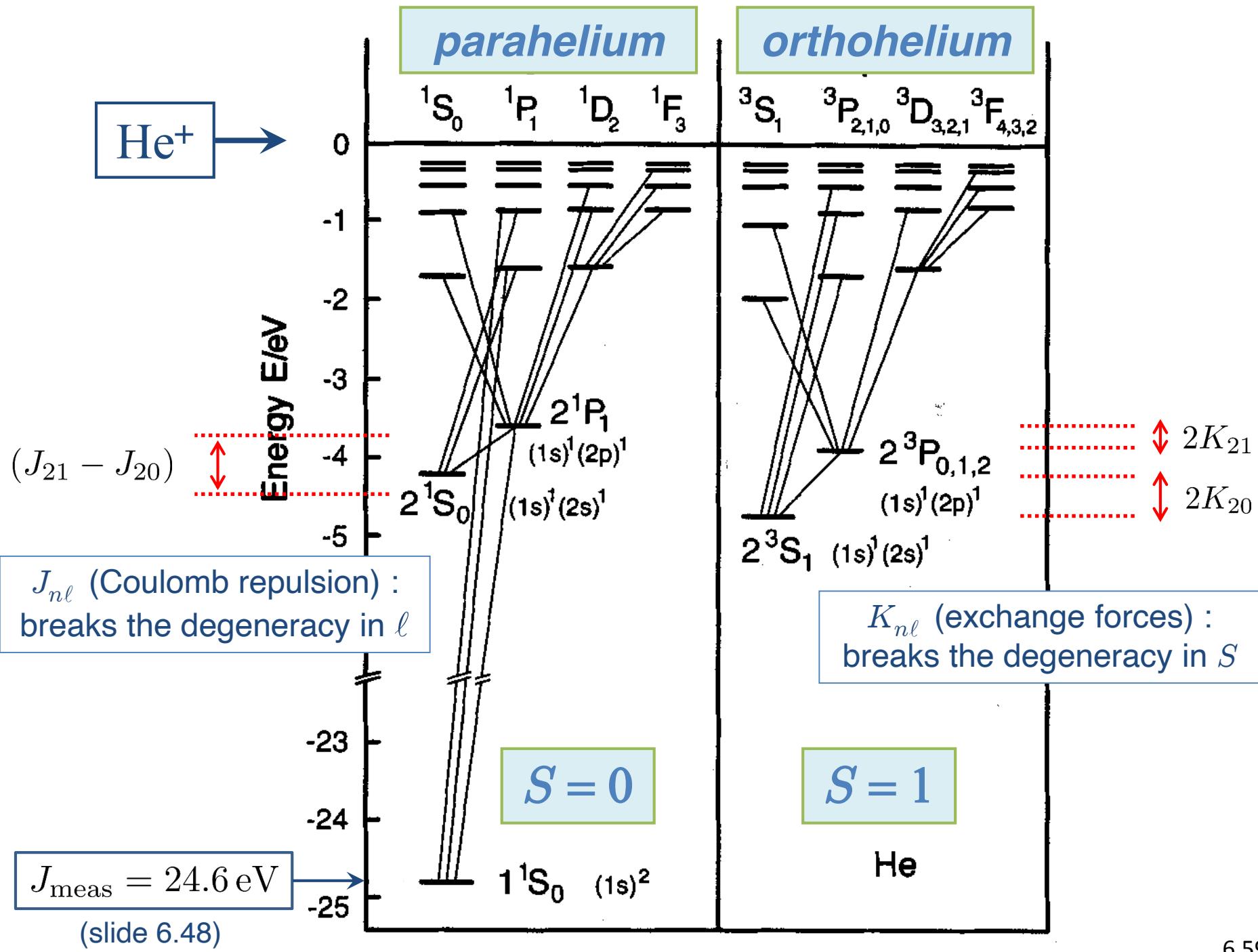
- The $K_{n\ell}$ term is an exchange contribution reflecting the antisymmetry of the overall wavefunction; it is also necessarily positive :

$$K_{n\ell} > 0$$

(The proof of this statement is given in Appendix B, for completeness)

- From equation (6.57.1), the $K_{n\ell}$ contribution gives a positive energy shift for parahelium ($S = 0$) and a negative energy shift for orthohelium ($S = 1$) :





Excited states of helium (5)

A qualitative explanation :

- States with $S = 1$ (orthohelium) have an antisymmetric spatial component of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2))$$

The wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$ therefore vanishes when $\mathbf{r}_1 = \mathbf{r}_2$;
the probability of finding the two electrons at the same position vanishes

- ⇒ the electrons tend to be further apart for $S = 1$ than for $S = 0$
- ⇒ the Coulomb energy is lower for $S = 1$ than for $S = 0$
- ⇒ the $S = 1$ states lie lower in energy than $S = 0$

- This is an example of an *exchange interaction* :
the Hamiltonian H does not involve the spin operators S_1 or S_2 ,
but despite this, the states $S = 0$ and $S = 1$ are *not* degenerate in energy

Electric Dipole Transitions in Helium

- For helium, the rate, Γ , for an electric dipole (E1) transition,

$$|\alpha\rangle \longleftrightarrow |\beta\rangle + \gamma$$

between atomic states $|\alpha\rangle$ and $|\beta\rangle$ is given by

$$\Gamma \propto \omega^3 |\langle \beta | \hat{\mathbf{d}} | \alpha \rangle|^2 ; \quad \hat{\mathbf{d}} = -e\hat{\mathbf{r}}_1 - e\hat{\mathbf{r}}_2$$

where the electric dipole operator \mathbf{d} is now a sum over the two electrons

- The operator \mathbf{d} does not involve the electron spin operators S_1 or S_2

Hence the spin component of the atomic state must remain unchanged in an E1 transition, as expressed by the selection rules

$$\boxed{\Delta S = 0 ; \quad \Delta m_S = 0}$$

- Thus parahelium ($S = 0$) and orthohelium ($S = 1$) form two completely separate spectroscopic systems

Helium : E1 transitions (2)

- Consider a transition (emission or absorption) between any two states of atomic helium :

$$(1s)(n\ell) \leftrightarrow (1s)(n'\ell')$$

- The spatial components of the wavefunctions for each state are of the form

$$\frac{1}{\sqrt{2}}(|100; n\ell m\rangle \pm |n\ell m; 100\rangle)$$

with “+” for $S = 0$ (parahelium), and “−” for $S = 1$ (orthohelium), and where the notation

$$|n\ell m; 100\rangle \equiv |n\ell m\rangle |100\rangle$$

has been introduced for the direct product of two single-particle states

- Evaluation of the dipole matrix element $\langle \beta | \hat{\mathbf{d}} | \alpha \rangle$ involves terms such as

$$\langle 100; n'\ell'm' | \hat{\mathbf{d}} | 100; n\ell m \rangle$$

$$= -e \langle 100; n'\ell'm' | \hat{\mathbf{r}}_1 | 100; n\ell m \rangle - e \langle 100; n'\ell'm' | \hat{\mathbf{r}}_2 | 100; n\ell m \rangle$$

$$= -e \langle 100 | \hat{\mathbf{r}}_1 | 100 \rangle \langle n'\ell'm' | n\ell m \rangle - e \langle 100 | 100 \rangle \langle n'\ell'm' | \hat{\mathbf{r}}_2 | n\ell m \rangle$$

Helium : E1 transitions (3)

- The matrix element factors $\langle 100 | \hat{\mathbf{r}}_1 | 100 \rangle$ and $\langle n' \ell' m' | \hat{\mathbf{r}}_2 | n \ell m \rangle$ above are the same as already considered for hydrogen (slide 5.53)

In particular, the first term on the right-hand side vanishes :

$$\langle 100 | \hat{\mathbf{r}}_1 | 100 \rangle = 0$$

This leaves

$$\langle 100 | 100 \rangle = 1$$

$$\langle 100; n' \ell' m' | \hat{\mathbf{d}} | 100; n \ell m \rangle = -e \langle n' \ell' m' | \hat{\mathbf{r}}_2 | n \ell m \rangle$$

- Thus the E1 selection rules obtained earlier for hydrogen continue to apply also for helium :

$$\Delta \ell = \pm 1 ; \quad \Delta m_\ell = 0, \pm 1$$

For example :

$(1s)(1s) \leftrightarrow (1s)(2p)$ is an allowed E1 transition

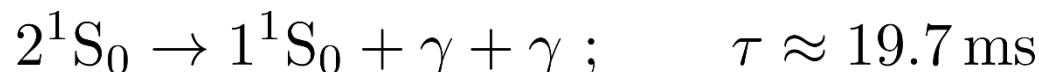
$(1s)(1s) \leftrightarrow (1s)(3d)$ is *not* allowed

- Parahelium and orthohelium therefore each have a spectrum of transitions which is hydrogen-like (see the Grotrian diagram on slide 6.59)

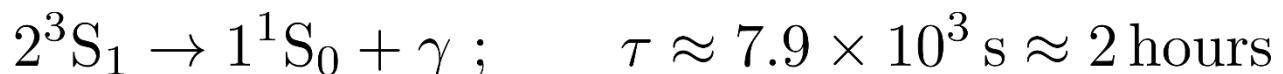
Helium : metastable states

- The (1s)(2s) states in each system have no available E1 decays open to them, and are therefore *metastable* :

$S = 0$: the 2^1S_0 state decays to the helium ground state by emitting two photons :



$S = 1$: the 2^3S_1 state decays to the helium ground state via a low rate decay which violates the $\Delta S = 0$ rule :



Helium : fine structure

- Finally, we briefly consider *fine structure* contributions to the helium atom

For *parahelium* ($S = 0$), there is no fine structure splitting, because each energy level corresponds to only a single value of J :

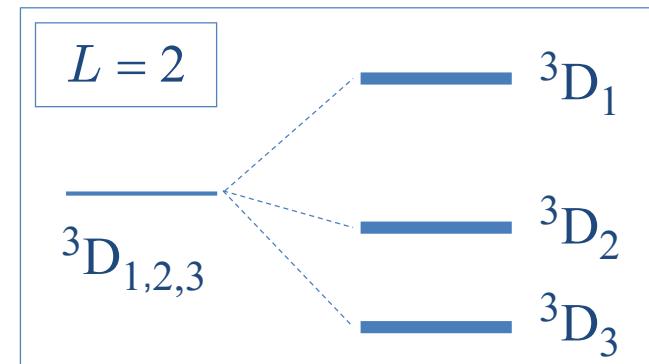
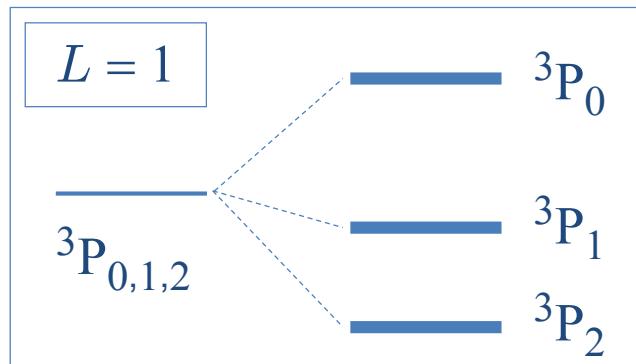
$$J = L \otimes S = L \otimes 0 = L$$

For *orthohelium* ($S = 1$), the possible J values for each energy level are

$$J = L \otimes S = L \otimes 1 = \begin{cases} L + 1, L, L - 1 & (L > 0) \\ 1 & (L = 0) \end{cases}$$

Thus, for $S = 1$ and $L > 0$, each level splits into three separate levels (one for each J) once fine structure effects are included

- e.g. :



Helium : fine structure (2)

- The operator \mathbf{d} is a vector operator ; hence electric dipole transitions between fine structure levels

$$|Jm_J\rangle_\beta \longleftrightarrow |Jm_J\rangle_\alpha$$

can only occur if they satisfy the selection rules

$$\boxed{\Delta J = 0, \pm 1 ; \quad J_\alpha + J_\beta \geq 1 ; \quad \Delta m_J = 0, \pm 1}$$

(in addition to the selection rules for $\Delta\ell$ and ΔS)

- The allowed (E1) spectral lines in $S = 0$ are all *singlets* :

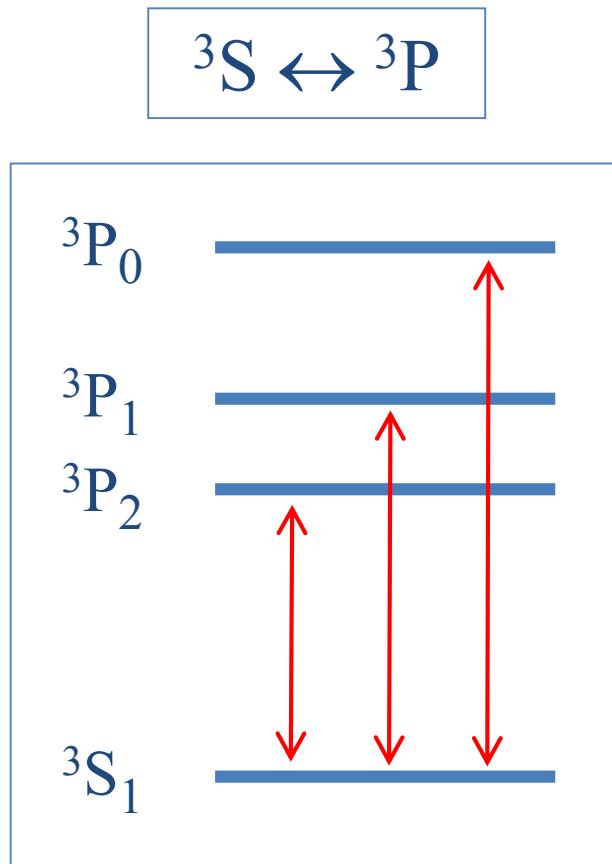
$$^1S_0 \leftrightarrow ^1P_1 ; \quad ^1P_1 \leftrightarrow ^1D_2 ; \quad ^1D_2 \leftrightarrow ^1F_3 ; \quad \dots$$

- The allowed spectral lines in $S = 1$ are all *multiplets* :

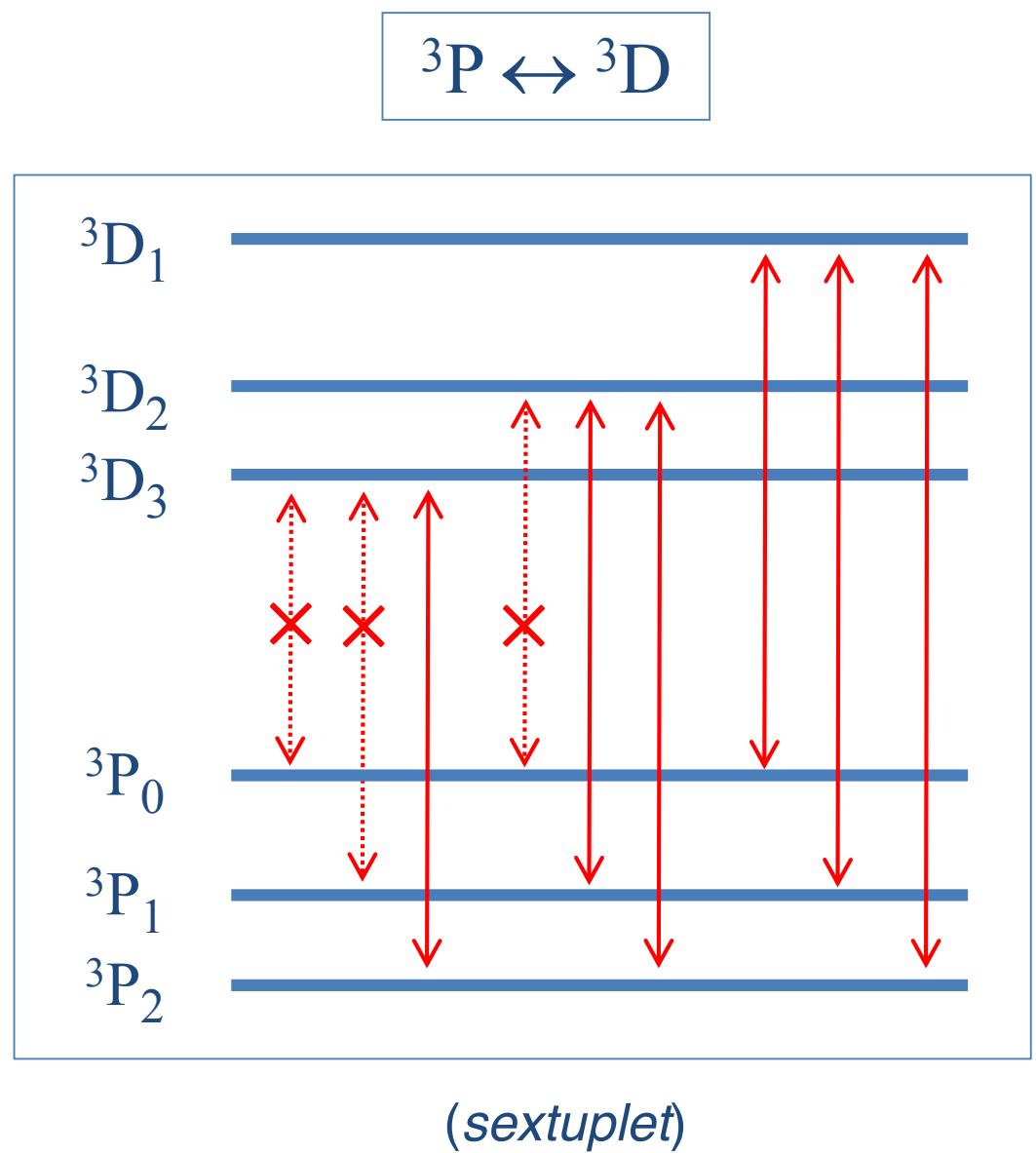
- transitions to the lowest energy state with $S = 1$, $^3S_1 \leftrightarrow ^3P_{2,1,0}$, are all *triplets*
- all other $S = 1$ transitions, such as $^3P_{2,1,0} \leftrightarrow ^3D_{3,2,1}$, are *sextuplets* (due to $\Delta J = \pm 1, 0$)

Helium : fine structure (3)

-- For example :



(triplet)



(sextuplet)

Helium Atom : Summary

- The helium atom consists of two spectroscopically distinct systems :
parahelium ($S = 0$) ; *orthohelium* ($S = 1$)
 - The effect of the $1/r_{12}$ Coulomb interaction can be estimated using the variational method, or perturbation theory
 - this breaks the degeneracy between states of different L
 - The two atomic electrons are identical fermions :
 - the helium ground state belongs to parahelium ($S = 0$)
 - exchange interactions lift the degeneracy in S for excited states ; orthohelium ($S = 1$) lies lower than parahelium ($S = 0$)
 - Taking fine structure into account lifts the degeneracy in J (for $S = 1$)
 - The ${}^4\text{He}$ nucleus (an α -particle) has zero spin
 - the helium atom has no hyperfine structure
- (but the isotope ${}^3\text{He}$ has spin $1/2$; the ${}^3\text{He}$ atom *does* have hyperfine structure)

Appendices

-- *Appendix A :*

Evaluation of the Coulomb integral (slide 6.44)

$$\iint \frac{e^{-(r_1+r_2)/r_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 20\pi^2 r_0^5$$

-- *Appendix B :*

Proof that the exchange contribution $K_{n\ell}$ is positive (slide 6.58)

$$K_{n\ell} > 0$$

Appendix A : the Coulomb integral

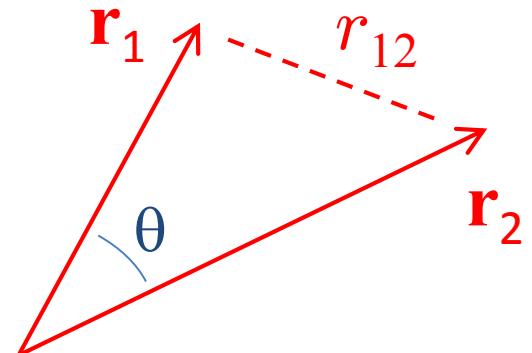
- The Coulomb interaction contribution E_{12} (slide 6.44) requires evaluation of the integral

$$\begin{aligned} I &\equiv \iint \frac{e^{-(r_1+r_2)/r_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 & d^3\mathbf{r}_1 &= r_1^2 dr_1 d\Omega_1 \\ &= \iint r_1^2 r_2^2 \frac{e^{-(r_1+r_2)/r_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} dr_1 dr_2 d\Omega_1 d\Omega_2 & d^3\mathbf{r}_2 &= r_2^2 dr_2 d\Omega_2 \end{aligned}$$

This is an integration over all possible positions of the two electrons

- Introducing the angle θ between the two position vectors, we can set

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta}}$$



The Coulomb integral (2)

- Choose the z axis to lie along the direction of \mathbf{r}_1 , so $d\Omega_2 = d\cos\theta d\phi$, and integrate over all possible directions of \mathbf{r}_2 :

$$\begin{aligned}\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\Omega_2 &= 2\pi \int_{-1}^{+1} \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}} d\cos\theta \\ &= 2\pi \left[-\frac{1}{r_1 r_2} \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta} \right]_{-1}^{+1} \\ &= -\frac{2\pi}{r_1 r_2} \left(\sqrt{r_1^2 + r_2^2 - 2r_1 r_2} - \sqrt{r_1^2 + r_2^2 + 2r_1 r_2} \right) \\ &= \frac{2\pi}{r_1 r_2} (r_1 + r_2 - |r_1 - r_2|)\end{aligned}$$

- Then the integral I is

$$\begin{aligned}I &= 2\pi \int r_1 r_2 e^{-(r_1 + r_2)/r_0} (r_1 + r_2 - |r_1 - r_2|) dr_1 dr_2 d\Omega_1 \\ &= 8\pi^2 \int_0^\infty \int_0^\infty r_1 r_2 e^{-(r_1 + r_2)/r_0} (r_1 + r_2 - |r_1 - r_2|) dr_1 dr_2\end{aligned}$$

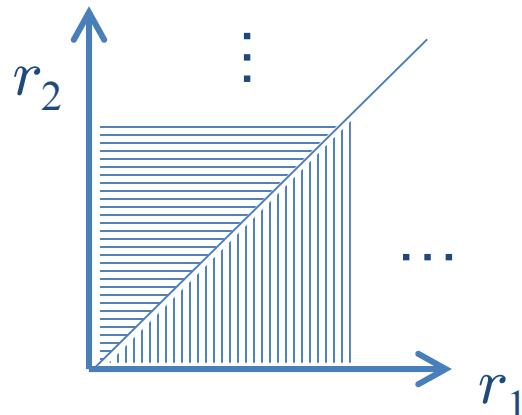
The Coulomb integral (3)

- We have

$$r_1 + r_2 - |r_1 - r_2| = \begin{cases} 2r_2 & (r_1 > r_2) \\ 2r_1 & (r_2 > r_1) \end{cases}$$

→ split the integration over (r_1, r_2) into two triangular regions :

$$\begin{aligned} I &= 8\pi^2 \int_0^\infty dr_1 \int_0^{r_1} dr_2 r_1 r_2 e^{-(r_1+r_2)/r_0} (2r_2) \\ &\quad + 8\pi^2 \int_0^\infty dr_2 \int_0^{r_2} dr_1 r_1 r_2 e^{-(r_1+r_2)/r_0} (2r_1) \end{aligned}$$



- Interchanging the integration variables, $r_1 \leftrightarrow r_2$, shows that the two terms above are equal :

$$\begin{aligned} I &= 2 \times 16\pi^2 \int_0^\infty dr_1 \int_0^{r_1} dr_2 r_1 r_2^2 e^{-(r_1+r_2)/r_0} \\ &= 32\pi^2 \int_0^\infty dr_1 r_1 e^{-r_1/r_0} \int_0^{r_1} dr_2 r_2^2 e^{-r_2/r_0} \end{aligned}$$

The Coulomb integral (4)

- Integration by parts gives the integral over r_2 as

$$\int_0^{r_1} dr_2 r_2^2 e^{-r_2/r_0} = -r_0(r_1^2 + 2r_0 r_1 + 2r_0^2) e^{-r_1/r_0} + 2r_0^3$$

Hence the integral I is

$$I = -32\pi^2 r_0 [I_3 + 2r_0 I_2 + 2r_0^2 I_1 - 2r_0^2 I']$$

where

$$I_n \equiv \int_0^\infty dr_1 r_1^n e^{-2r_1/r_0}; \quad I' \equiv \int_0^\infty dr_1 r_1 e^{-r_1/r_0}$$

are standard integrals :

$$I_3 = 6 \left(\frac{r_0}{2}\right)^4; \quad I_2 = 2 \left(\frac{r_0}{2}\right)^3; \quad I_1 = \left(\frac{r_0}{2}\right)^2; \quad I' = r_0^2$$

- Hence we finally obtain

$$I \equiv \iint \frac{e^{-(r_1+r_2)/r_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 20\pi^2 r_0^5$$

Appendix B : the exchange contribution

- The exchange term $K_{n\ell}$ was introduced on slide 6.57 as

$$K_{n\ell} = \frac{e^2}{4\pi\epsilon_0} \int \frac{\psi_{100}^*(\mathbf{r}_1)\psi_{n\ell 0}^*(\mathbf{r}_2)\psi_{100}(\mathbf{r}_2)\psi_{n\ell 0}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

- Introducing the quantity $\rho(\mathbf{r})$ defined as

$$\rho(\mathbf{r}) \equiv \psi_{100}(\mathbf{r})\psi_{n\ell 0}(\mathbf{r})$$

we can write $K_{n\ell}$ as (note that ψ is real for $m = 0$)

$$K_{n\ell} = \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \int d^3\mathbf{r}_2 \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- Poisson's equation for a source $\rho(\mathbf{r})$,

$$\nabla^2 \Phi(\mathbf{r}) = -\rho(\mathbf{r})$$

has the formal solution

$$\Phi(\mathbf{r}) = \frac{1}{4\pi} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

Exchange contribution (2)

- Hence $K_{n\ell}$ is of the form

$$K_{n\ell} = \frac{e^2}{\epsilon_0} \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \Phi(\mathbf{r}_1)$$

where $\Phi(\mathbf{r})$ is a solution of

$$\nabla^2 \Phi(\mathbf{r}) = -\rho(\mathbf{r})$$

$$\Rightarrow K_{n\ell} = -\frac{e^2}{\epsilon_0} \int d^3\mathbf{r}_1 \nabla^2 \Phi(\mathbf{r}_1) \Phi(\mathbf{r}_1) = -\frac{e^2}{\epsilon_0} \int d^3\mathbf{r} \Phi(\mathbf{r}) \nabla^2 \Phi(\mathbf{r})$$

- Integrating by parts gives

$$K_{n\ell} = \frac{e^2}{\epsilon_0} \int d^3\mathbf{r} (\nabla \Phi(\mathbf{r})) \cdot (\nabla \Phi(\mathbf{r})) - \frac{e^2}{\epsilon_0} \int d^3\mathbf{r} \nabla \cdot (\Phi(\mathbf{r}) \nabla \Phi(\mathbf{r}))$$

- The final term on the right-hand side can be converted to a surface integral using Gauss' theorem :

$$\int d^3\mathbf{r} \nabla \cdot (\Phi(\mathbf{r}) \nabla \Phi(\mathbf{r})) = \int (\Phi(\mathbf{r}) \nabla \Phi(\mathbf{r})) \cdot d\mathbf{S}$$

This surface integral vanishes, because $\Phi(\mathbf{r}) \rightarrow 0$ at infinity

Exchange contribution (3)

-- This leaves

$$K_{n\ell} = \frac{e^2}{\epsilon_0} \int d^3\mathbf{r} (\nabla\Phi(\mathbf{r})) \cdot (\nabla\Phi(\mathbf{r}))$$

The integral on the right-hand side is clearly positive; hence, as advertised :

$$K_{n\ell} > 0$$