



Lectures #8 - 9

Identical particles

Bosons and fermions

Slater determinants

Evaluation of one and two-particle matrix elements

Helium atom:

Applications of perturbation theory and

Variational method

Chapter 10, pages 469-477, 485-492 Quantum Mechanics

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Identical particles: example

Ground state of He atom: $1s^2$

Quantum numbers

1s

$$n=1$$

$$l=0$$

$$m_l=0$$

$$s=1/2$$

$$m_s=\pm 1/2$$

$1s^2$

$$L=0$$

$$M_L=0$$

$$S=0$$

$$M_S=0$$

Term: 1S

1s

$$n=1$$

$$l=0$$

$$m_l=0$$

$$s=1/2$$

$$m_s=\pm 1/2$$

No triplet 3S term for the $1s^2$ configuration

Quantum mechanical system of N-particle system

Quantum mechanical system of N particles is described by a wave function $\Psi(q_1, q_2, \dots, q_n, t)$

q_i : a complete set of commuting observables for particle i

$$i\hbar \frac{\partial}{\partial t} \Psi(q_1, q_2, \dots, q_N, t) = H \Psi(q_1, q_2, \dots, q_N, t)$$

$$H = -\sum_{i=1}^N \hbar^2 \frac{\nabla_i^2}{2m_i} + V$$

Lets consider time-independent potentials

$$\Psi(q_1, q_2, \dots, q_N, t) = \psi(q_1, q_2, \dots, q_N) e^{-iEt/\hbar}$$

Total energy of the system

Solutions of $H\psi = E\psi$

The total orbital angular momentum

$$\mathbf{L} = \sum_{i=1}^N \mathbf{L}_i$$

The total spin angular momentum

$$\mathbf{S} = \sum_{i=1}^N \mathbf{S}_i$$

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$



N-particle system: a special case

No interaction between any pair of particles

Each particle may interact with external potential

$$H = \sum_{i=1}^N h_i$$

Single-particle Hamiltonians

$$h_i \psi_a(q_i) = \varepsilon_a \psi_a(q_i)$$

$$H\Psi(q_1, q_2, \dots, q_N) = E\Psi(q_1, q_2, \dots, q_N)$$

$$\Psi(q_1, \dots, q_n) = \psi_a(q_1)\psi_b(q_2)\dots\psi_n(q_N)$$

$$E = \varepsilon_a + \varepsilon_b + \dots + \varepsilon_n$$



Uncorrelated system

Systems of identical particles

Two particles are considered identical if they can not be distinguished by means of any intrinsic property.

$$\Psi(q_1, q_2, \dots, q_i, \dots, q_j, \dots, q_N)$$

P_{ij}

All observables must be symmetric with respect to $q_i \rightleftharpoons q_j$ interchange as N particles are identical

$P_{ij}\Psi$ is also an eigenfunction of H

$$[H, P_{ij}] = 0$$

$$P_{ij}\Psi(q_1, q_2, \dots, q_i, \dots, q_j, \dots, q_N) = \Psi(q_1, q_2, \dots, q_j, \dots, q_i, \dots, q_N)$$



Systems of identical particles

$$P_{ij}\Psi(q_1, q_2, \dots, \mathbf{q}_i, \dots, \mathbf{q}_j, \dots, q_N) = \Psi(q_1, q_2, \dots, \mathbf{q}_j, \dots, \mathbf{q}_i, \dots, q_N)$$

$$P_{ij}^2 = 1 \longrightarrow \text{Eigenvalues } \varepsilon \text{ of } P_{ij} \text{ are } \varepsilon = \pm 1$$

$\varepsilon = 1$: **Symmetric** wave functions under P_{ij} interchange

$$P_{ij}\Psi(q_1, q_2, \dots, \mathbf{q}_i, \dots, \mathbf{q}_j, \dots, q_N) = \Psi(q_1, q_2, \dots, \mathbf{q}_i, \dots, \mathbf{q}_j, \dots, q_N)$$

$\varepsilon = -1$: **Antisymmetric** wave functions under P_{ij} interchange

$$P_{ij}\Psi(q_1, q_2, \dots, \mathbf{q}_i, \dots, \mathbf{q}_j, \dots, q_N) = -\Psi(q_1, q_2, \dots, \mathbf{q}_i, \dots, \mathbf{q}_j, \dots, q_N)$$



Symmetric and antisymmetric wave functions

There are $N!$ different permutations

$$P\Psi(q_1, q_2, \dots, q_N) = \Psi(q_{P1}, q_{P2}, \dots, q_{PN})$$

Totally symmetric state

$$P\Psi_S(q_1, \dots, q_N) = \Psi_S(q_1, \dots, q_N)$$

Totally antisymmetric state

$$P\Psi_A(q_1, \dots, q_N) = \begin{cases} \Psi_A(q_1, \dots, q_N) & \text{for even permutations} \\ -\Psi_A(q_1, \dots, q_N) & \text{for odd permutations} \end{cases}$$

for any interchange P_{ij}



Bosons and fermions

Symmetrisation postulate:
all systems of identical particles can be described
by either Ψ_A or Ψ_S states.

Bosons

$$\Psi_S$$

Spin: zero or integer

0, 1, 2, ...

Bose–Einstein
statistics

Fermions

$$\Psi_A$$

Spin: half – integer

1/2, 3/2, ...

Fermi–Dirac
statistics



How to construct Ψ_A and Ψ_S ?

N=2

$$\Psi_S(q_1, q_2) = \frac{1}{\sqrt{2}} \{ \psi(q_1, q_2) + \psi(q_2, q_1) \}$$

$$\Psi_A(q_1, q_2) = \frac{1}{\sqrt{2}} \{ \psi(q_1, q_2) - \psi(q_2, q_1) \}$$

N=3

$$\begin{aligned} \Psi_S(q_1, q_2, q_3) = \frac{1}{\sqrt{6}} \{ & \psi(q_1, q_2, q_3) + \psi(q_2, q_3, q_1) + \psi(q_3, q_1, q_2) \\ & + \psi(q_2, q_1, q_3) + \psi(q_1, q_3, q_2) + \psi(q_3, q_2, q_1) \} \end{aligned}$$

$$\begin{aligned} \Psi_A(q_1, q_2, q_3) = \frac{1}{\sqrt{6}} \{ & \psi(q_1, q_2, q_3) + \psi(q_2, q_3, q_1) + \psi(q_3, q_1, q_2) \\ & - \psi(q_2, q_1, q_3) - \psi(q_1, q_3, q_2) - \psi(q_3, q_2, q_1) \} \end{aligned}$$

Again, a special case: $H = \sum_{i=1}^N h_i$

N=2

$$\Psi_S(q_1, q_2) = \frac{1}{\sqrt{2}} \{ \psi_a(q_1) \psi_b(q_2) + \psi_a(q_2) \psi_b(q_1) \}$$

$$\Psi_A(q_1, q_2) = \frac{1}{\sqrt{2}} \{ \psi_a(q_1) \psi_b(q_2) - \psi_a(q_2) \psi_b(q_1) \}$$

Note: these wave functions can not be represented as products of single-particles states, i.e. they are entangled

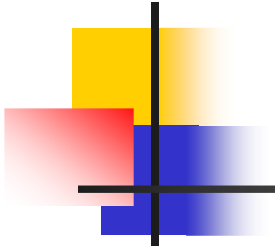
N

$$\Psi_A(q_1, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(q_1) & \psi_b(q_1) & \cdots & \psi_n(q_1) \\ \psi_a(q_2) & \psi_b(q_2) & \cdots & \psi_n(q_2) \\ \vdots & \vdots & & \vdots \\ \psi_a(q_N) & \psi_b(q_N) & \cdots & \psi_n(q_N) \end{vmatrix}$$

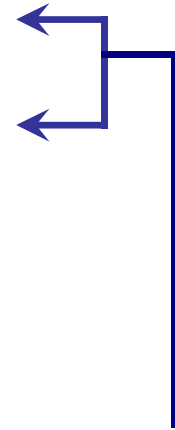
← Slater determinant

$\Psi_S(q_1, \dots, q_N)$ is obtained by expanding the determinant and changing all signs to “+”

Slater determinants & Pauli exclusion principle



$$\Psi_A(q_1, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(q_1) & \psi_b(q_1) & \cdots & \psi_n(q_1) \\ \psi_a(q_2) & \psi_b(q_2) & \cdots & \psi_n(q_2) \\ \vdots & \vdots & & \vdots \\ \psi_a(q_N) & \psi_b(q_N) & \cdots & \psi_n(q_N) \end{vmatrix}$$



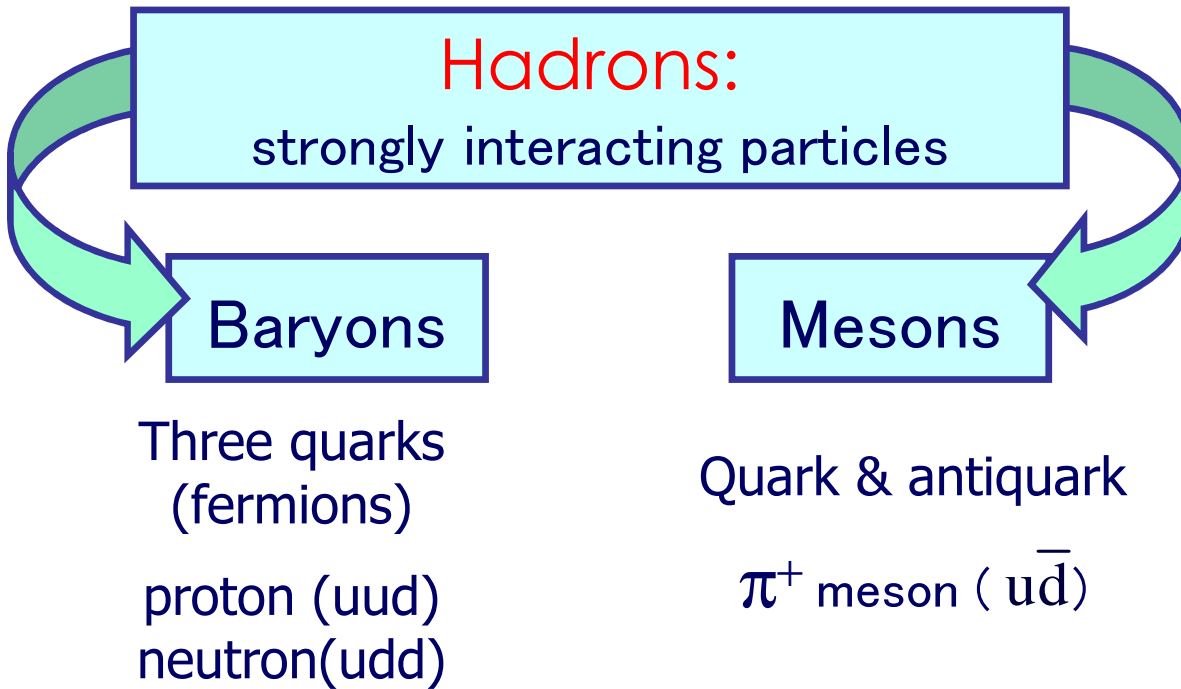
Interchanging of the two rows changes sign of the determinant: the function is completely antisymmetric

If any of the two particles are identical \Rightarrow two columns are the same and the determinant is equal zero.

Pauli exclusion principle

Only one fermion can occupy a certain quantum state.

The Pauli exclusion principle, quarks & colors



u and d quarks

flavor	charge	spin
u ("up")	$2/3e$	$1/2$
d ("down")	$-1/3e$	$1/2$

Δ^{++} baryon: spin $J=3/2$, charge $2e$
expected to be (uuu)

But that will violate Pauli exclusion principle!

Quarks must have extra
internal quantum number:
color and each of the three
quarks has different color

System of N particles: many-particle operators

$$F = \sum_{i=1}^N f(\mathbf{r}_i)$$

← One-particle operators

Example: $H = \sum_{i=1}^N h_i$

Lets designate our Slater determinate functions $\Psi_{ab\dots n}$

How to evaluate the corresponding matrix elements?

$$\langle \Psi_{a'b'\dots n'} | F | \Psi_{ab\dots n} \rangle = 0$$

If the indices $\{a'b'\dots n'\}$ and $\{ab\dots n\}$ differ in more than one place

$$\langle \Psi_{a'b'\dots n'} | F | \Psi_{ab\dots n} \rangle = f_{k'k}$$

If only the indices k and k' differ

$$\langle \Psi_{a'b'\dots n'} | F | \Psi_{ab\dots n} \rangle = \sum_{i=a}^N f_{ii}$$

If the sets of indices $\{a'b'\dots n'\}$ and $\{ab\dots n\}$ are the same.

$$f_{ab} = \langle a | f | b \rangle = \int d^3r \psi_a^\dagger(\mathbf{r}) f(\mathbf{r}) \psi_b(\mathbf{r})$$

System of N particles: many-particle operators

$$G = \frac{1}{2} \sum_{i \neq j} g(r_{ij})$$

Two-particle operators

Example: $\frac{1}{r_{12}}$

$$\langle \Psi_{a'b' \dots n'} | G | \Psi_{ab \dots n} \rangle = 0$$

If the indices $\{a'b' \dots n'\}$ and $\{ab \dots n\}$ differ in more than two places

$$\langle \Psi_{a'b' \dots n'} | G | \Psi_{ab \dots n} \rangle = g_{k'l'kl} - g_{k'l'lk}$$

If only the pairs of indices kl and $k'l'$ differ

$$\langle \Psi_{a'b' \dots n'} | G | \Psi_{ab \dots n} \rangle = \sum_{i=a}^n (g_{k'iki} - g_{k'iiik})$$

If only the indices k and k' differ

$$\langle \Psi_{a'b' \dots n'} | G | \Psi_{ab \dots n} \rangle = \frac{1}{2} \sum_{i,j} (g_{ijij} - g_{ijji})$$

If the sets of indices $\{a'b' \dots n'\}$ and $\{ab \dots n\}$ are the same.

$$g_{abcd} = \langle ab | g | cd \rangle = \int d^3 r_1 \int d^3 r_2 \psi_a^\dagger(\mathbf{r}_1) \psi_b^\dagger(\mathbf{r}_2) g(\mathbf{r}_{12}) \psi_c(\mathbf{r}_1) \psi_d(\mathbf{r}_2)$$



Two-electron systems

Z=2: He

Z=3: Li⁺

Z=4: Be⁺⁺

...

Origin of the coordinate system: nucleus, \mathbf{r}_1 and \mathbf{r}_2
are the position vectors of the two electrons

$$H = H_0 + H'$$

$$H_0 = h_1 + h_2$$
$$h_i = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{(4\pi\epsilon_0)r_i}$$

$$H' = \frac{e^2}{(4\pi\epsilon_0)r_{12}}$$

In atomic units:

$$H = \sum_{i=1,2} \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \frac{1}{r_{12}}$$

Z=2: He

Z=3: Li⁺

Z=4: Be⁺⁺

...

Two-electron wave functions

$$H = \sum_{i=1,2} \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \frac{1}{r_{12}}$$

$$H\Psi(q_1, q_2) = E\Psi(q_1, q_2)$$

$$\Psi(q_1, q_2) = \phi(\mathbf{r}_1, \mathbf{r}_2) \chi_{S, M_S}(1, 2)$$

← Eigenvalues of $\{H, \mathbf{L}^2, L_z, \mathbf{S}^2, S_z\}$

Lets introduce space-symmetric and space-antisymmetric wave functions:

$$\phi^+(\mathbf{r}_1, \mathbf{r}_2) = \phi^+(\mathbf{r}_2, \mathbf{r}_1)$$

$$\phi^-(\mathbf{r}_1, \mathbf{r}_2) = -\phi^-(\mathbf{r}_2, \mathbf{r}_1)$$

Need to construct symmetric and antisymmetric spin functions

Z=2: He

Z=3: Li⁺

Z=4: Be⁺⁺

Two-electron wave functions

$$s_1 = 1/2 \text{ and } s_2 = 1/2 \rightarrow \begin{cases} S = 0 \quad M_s = 0 & \text{singlet state (antisymmetric)} \\ S = 1 \quad M_s = 0, \pm 1 & \text{triplet state (symmetric)} \end{cases}$$

Lets construct the corresponding symmetric and antisymmetric spin functions

$$|SM_s\rangle = |11\rangle = |\frac{1}{2} \frac{1}{2}, \frac{1}{2} \frac{1}{2}\rangle \quad |1-1\rangle = |\frac{1}{2} -\frac{1}{2}, \frac{1}{2} -\frac{1}{2}\rangle$$

$$S_- |11\rangle = \sqrt{2} |10\rangle = |\frac{1}{2} \frac{1}{2}, \frac{1}{2} -\frac{1}{2}\rangle + |\frac{1}{2} -\frac{1}{2}, \frac{1}{2} \frac{1}{2}\rangle$$

$$|10\rangle = \frac{1}{\sqrt{2}} \{ |\frac{1}{2} \frac{1}{2}, \frac{1}{2} -\frac{1}{2}\rangle + |\frac{1}{2} -\frac{1}{2}, \frac{1}{2} \frac{1}{2}\rangle \}$$

$$|00\rangle = a |\frac{1}{2} \frac{1}{2}, \frac{1}{2} -\frac{1}{2}\rangle + b |\frac{1}{2} -\frac{1}{2}, \frac{1}{2} \frac{1}{2}\rangle$$

$$\langle 10|00\rangle = 0 \rightarrow b = -a; \quad \langle 00|00\rangle = 1 \rightarrow 2a^2 = 1 \rightarrow a = \frac{1}{\sqrt{2}}$$

$$|00\rangle = \frac{1}{\sqrt{2}} \{ |\frac{1}{2} \frac{1}{2}, \frac{1}{2} -\frac{1}{2}\rangle - |\frac{1}{2} -\frac{1}{2}, \frac{1}{2} \frac{1}{2}\rangle \}$$

Z=2: He

Z=3: Li⁺

Z=4: Be⁺⁺

...

Two-electron wave functions

Electrons are fermions: the total wave function must be antisymmetric

Space-symmetric

Spin singlet state (antisymmetric)

$$\Psi^{S=0}(q_1, q_2) = \phi^+(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{\sqrt{2}} \left\{ \left| \frac{1}{2} \frac{1}{2}, \frac{1}{2} -\frac{1}{2} \right\rangle - \left| \frac{1}{2} -\frac{1}{2}, \frac{1}{2} \frac{1}{2} \right\rangle \right\}$$

Antisymmetric

$$\Psi^{S=1}(q_1, q_2) = \phi^-(\mathbf{r}_1, \mathbf{r}_2) \times \begin{cases} \left| \frac{1}{2} \frac{1}{2}, \frac{1}{2} \frac{1}{2} \right\rangle \\ \frac{1}{\sqrt{2}} \left\{ \left| \frac{1}{2} \frac{1}{2}, \frac{1}{2} -\frac{1}{2} \right\rangle + \left| \frac{1}{2} -\frac{1}{2}, \frac{1}{2} \frac{1}{2} \right\rangle \right\} \\ \left| \frac{1}{2} -\frac{1}{2}, \frac{1}{2} -\frac{1}{2} \right\rangle \end{cases}$$

Space-antisymmetric

Spin triplet state (symmetric)

Ground state: identical electrons

Z=2: He

Z=3: Li⁺

Z=4: Be⁺⁺

Space-symmetric

Spin singlet state (anti-symmetric)

$$\Psi^{S=0}(q_1, q_2) = \phi^+(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{\sqrt{2}} \left\{ \left| \frac{1}{2} \frac{1}{2}, \frac{1}{2} - \frac{1}{2} \right\rangle - \left| \frac{1}{2} - \frac{1}{2}, \frac{1}{2} \frac{1}{2} \right\rangle \right\}$$

Antisymmetric

Spin triplet state (symmetric)

$$\Psi^{S=1}(q_1, q_2) = \phi^-(\mathbf{r}_1, \mathbf{r}_2) \times \begin{cases} \left| \frac{1}{2} \frac{1}{2}, \frac{1}{2} \frac{1}{2} \right\rangle \\ \frac{1}{\sqrt{2}} \left\{ \left| \frac{1}{2} \frac{1}{2}, \frac{1}{2} - \frac{1}{2} \right\rangle + \left| \frac{1}{2} - \frac{1}{2}, \frac{1}{2} \frac{1}{2} \right\rangle \right\} \\ \left| \frac{1}{2} - \frac{1}{2}, \frac{1}{2} - \frac{1}{2} \right\rangle \end{cases}$$

Space-antisymmetric
function is zero if
particles are identical

There is no triplet state for
1s² configuration.

Ground state: identical electrons

Z=2: He

Z=3: Li⁺

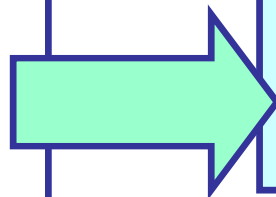
Z=4: Be⁺⁺

...

Ground state of He (or He-like ion): $1s^2 \ ^1S$

$$\Psi^{S=0}(q_1, q_2) = \phi^+(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{\sqrt{2}} \left\{ \left| \frac{1}{2} \frac{1}{2}, \frac{1}{2} - \frac{1}{2} \right\rangle - \left| \frac{1}{2} - \frac{1}{2}, \frac{1}{2} \frac{1}{2} \right\rangle \right\}$$

Space-antisymmetric
function is zero if
particles are identical



There is no triplet state for
 $1s^2$ configuration.

Two-electron systems: Lowest order

Z=2: He

Z=3: Li⁺

Z=4: Be⁺⁺

...

$$H_0 = h_1 + h_2$$

$$h_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}$$

$$h_i \psi_a(\mathbf{r}_i) = \varepsilon_a \psi_a(\mathbf{r}_i)$$

Solutions: Coulomb (H-like) wave functions

$$\psi_{nlm}(\mathbf{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \phi)$$

$$\varepsilon_n = -\frac{Z^2}{2n^2} \text{ (in a.u.)}$$

Note: 1 a.u. of
energy is ≈ 27.2 eV

Lowest order:

$$\phi_{\pm}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2)$$

“ \pm ”: space-(anti)symmetric
wave functions

$$E_0 = -\frac{Z^2}{2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \text{ (in a.u.)}$$

$$1s^2 : n_1 = n_2 = 1 \quad E^{(0)} = -Z^2$$

Ground state:

$$\text{He (Z = 2): } E_{1s1s}^{(0)} = -4 \text{ a.u.} \approx -4 \times 27.2 \text{ eV} = -109 \text{ eV}$$



Two-electron systems: Perturbation theory

$Z=2$: He

$Z=3$: Li^+

$Z=4$: Be^{++}

...

Lowest order:

$$E_0 = -\frac{Z^2}{2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \text{ (in a.u.)}$$

$$1s^2 : n_1 = n_2 = 1 \quad E^{(0)} = -Z^2$$

Ground state: He ($Z = 2$): $E_{1s1s}^{(0)} = -4 \text{ a.u.} \approx -4 \times 27.2 \text{ eV} = -109 \text{ eV}$

$$E_{1s1s}^{expt} \approx -79 \text{ eV}$$

Not a very good result!
Lets calculate first order energy:

$$E^{(1)} = \langle \Psi^{(0)} | H' | \Psi^{(0)} \rangle$$

Z=2: He

Z=3: Li⁺

Z=4: Be⁺⁺

...

First-order energy

$$E^{(1)} = \langle \Psi^{(0)} | H' | \Psi^{(0)} \rangle$$

$$H' = \frac{1}{r_{12}}$$

Single-electron (hydrogenic) wave functions are $\psi_{1s}(r) = \frac{1}{\sqrt{4\pi}} 2Z^{3/2} e^{-Zr}$.

Normalized lowest-order space-symmetric two-electron wave function is:

$$\phi_+^{(0)}(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2) = \frac{1}{\pi} Z^3 e^{-Z(r_1+r_2)}$$

$$E^{(1)} = \int |\phi_+^{(0)}(r_1, r_2)|^2 \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad \text{What to do with } \frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} ?$$



Irreducible tensor operators

Coulomb interaction

$1/r_{12}$ can be expanded in partial waves

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \theta)$$

Legendre polynomial

$r_{<}$ and $r_{>}$ are lesser
and greater of r_1, r_2
 θ is the angle
between the vectors
 r_1 and r_2

$$P_k(\cos \theta) = \frac{4\pi}{2k+1} \sum_{q=-k}^k Y_{kq}^*(\theta_1, \phi_1) Y_{kq}(\theta_2, \phi_2)$$

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_{<}^k}{r_{>}^{k+1}} \sum_{q=-k}^k Y_{kq}^*(\theta_1, \phi_1) Y_{kq}(\theta_2, \phi_2)$$

$r_<$ and $r_>$ are lesser and greater of r_1, r_2

First-order energy

$$E^{(1)} = \int \left| \phi_+^{(0)}(r_1, r_2) \right|^2 \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^k Y_{kq}^*(\theta_1, \phi_1) Y_{kq}(\theta_2, \phi_2)$$

$$= \int \left| \phi_+^{(0)}(r_1, r_2) \right|^2 \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^k Y_{kq}^*(\theta_1, \phi_1) Y_{kq}(\theta_2, \phi_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \frac{4\pi}{2k+1} \sum_{k=0}^{\infty} \sum_{q=-k}^k \int_0^{\infty} dr_1 r_1^2 \int_0^{\infty} dr_2 r_2^2 \frac{r_<^k}{r_>^{k+1}} \left| \phi_+^{(0)}(r_1, r_2) \right|^2 \underbrace{\int d\Omega_1 Y_{kq}^*(\theta_1, \phi_1) \int d\Omega_2 Y_{kq}(\theta_2, \phi_2)}_{\text{How to integrate over } d\Omega_1 \text{ and } d\Omega_2?}$$

Note: $\phi_+^{(0)}(r_1, r_2)$ is spherically symmetric

How to integrate over $d\Omega_1$ and $d\Omega_2$?

Lets multiply our expression by $4\pi Y_{00} Y_{00}$, $Y_{00} = \frac{1}{\sqrt{4\pi}}$.

$r_<$ and $r_>$ are lesser
and greater of r_1, r_2

First-order energy

$$\int d\Omega_1 Y_{kq}^*(\theta_1, \phi_1) \int d\Omega_2 Y_{kq}(\theta_2, \phi_2) = 4\pi \int d\Omega_1 Y_{kq}^*(\theta_1, \phi_1) Y_{00} \int d\Omega_2 Y_{kq}(\theta_2, \phi_2) Y_{00}$$

The spherical harmonics are orthonormal on the unit sphere:

$$\int d\Omega Y_{k'q'}^*(\theta, \phi) Y_{kq}(\theta, \phi) = \delta_{kk'} \delta_{qq'}$$

Therefore: $\int d\Omega_1 Y_{kq}^*(\theta_1, \phi_1) Y_{00} = \delta_{k0} \delta_{q0}$ and only one term $k=0$ $q=0$ contributes from the sums over k and q .

$$E^{(1)} = (4\pi)^2 \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 \frac{1}{r_>} |\phi_+^{(0)}(r_1, r_2)|^2 = 16Z^6 \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 \frac{1}{r_>} e^{-2Z(r_1+r_2)} = (*)$$

$r_<$ and $r_>$ are lesser and greater of r_1, r_2

First-order energy

$$\begin{aligned}
 (*) &= 16Z^6 \int_0^\infty dr_1 r_1^2 \left\{ \int_0^{r_1} r_2^2 dr_2 \frac{1}{r_1} e^{-2Z(r_1+r_2)} + \int_{r_1}^\infty r_2^2 dr_2 \frac{1}{r_2} e^{-2Z(r_1+r_2)} \right\} \\
 &= 16Z^6 \left\{ \int_0^\infty dr_1 r_1 e^{-2Zr_1} \int_0^{r_1} r_2^2 dr_2 e^{-2Zr_2} + \int_0^\infty dr_1 r_1^2 e^{-2Zr_1} \int_{r_1}^\infty r_2 dr_2 e^{-2Zr_2} \right\} = \frac{5}{8} Z
 \end{aligned}$$

We used Maple to evaluate this integral

$$\left. \begin{aligned}
 &> \text{assume}(Z>0): \\
 &> s1:=\text{int}(r2*r2*\exp(-2*Z*r2),r2=0..r1): \\
 &> s2:=\text{int}(r2*\exp(-2*Z*r2),r2=r1..infinity): \\
 &> 16*Z^6*\text{int}(r1*\exp(-2*Z*r1)*s1+r1*r1*\exp(-2*Z*r1)*s2,r1=0..infinity);
 \end{aligned} \right\} \frac{5Z}{8}$$



He ground state energy

$$\text{He: } (Z = 2) \quad E^{(1)} = \frac{5}{4} a.u. \approx 34 \text{ eV}$$

$$E = E^{(0)} + E^{(1)} = -109 + 34 = -75 \text{ eV} \text{ vs. } E^{\text{expt}} = -79 \text{ eV}$$

Much better agreement!
5% instead of 38%

Can we improve it without calculating the second order?
We can try to use the variational method.



He ground state energy: Rayleigh-Ritz variational method

$$E[\phi] = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

ϕ is a trial function depending on the variational parameters $\lambda_1, \lambda_2, \dots$. The optimum ground-state energy is obtained by minimizing $E(\lambda_1, \lambda_2, \dots)$ with respect to the parameters λ .

$$\text{Trial function: } \phi(\lambda, r_1, r_2) = \frac{1}{\pi} \lambda^3 e^{-\lambda(r_1+r_2)} \quad \langle \phi | \phi \rangle = 1$$

$$H = \sum_{i=1,2} \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \frac{1}{r_{12}}$$

$$E[\phi] = \lambda^2 - 2Z\lambda + \frac{5}{8}\lambda; \quad \frac{dE}{d\lambda} = 0 \rightarrow \lambda = Z - \frac{5}{16}$$

↑
Same is previous calculation of first-order energy with $Z=\lambda$



He isoelectronic sequence

$$E^{(0)} = -Z^2$$

$$E^{(0)} + E^{(1)} = -Z^2 + \frac{5}{8}Z$$

$$E_{\text{var}} = -\left(Z - \frac{5}{16}\right)^2$$

Difference with accurate values

	Z	$E^{(0)}$	$E^{(0)} + E^{(1)}$	E_{var}
He	2	38%	5%	2%
Li ⁺	3	24%	2%	0.7%
Be ²⁺	4	17%	1.2%	0.5%
B ³⁺	5	13%	0.7%	0.3%
C ⁴⁺	6	11%	0.5%	0.2%