

5. Two and Many-Electron Atoms

nuclei: fixed

$$H = \sum_i H_i + \sum_{i < j} \frac{e^2}{|R_i - R_j|} + \text{spin-orbit} + \dots$$

$$H_i = T_i + V_i = \frac{P_i^2}{2m_e} - \frac{Z e^2}{R_i}$$

[use lower case r]

cannot be solved analytically in Schrödinger picture.

Simplest Treatment: Independent Electron Approximation

Ignore electron-electron repulsion!

$$H = \sum_i H_i \Rightarrow \Psi = \prod_i \phi_i (r_i, \sigma_i, \phi_i) | \pm \rangle_i$$

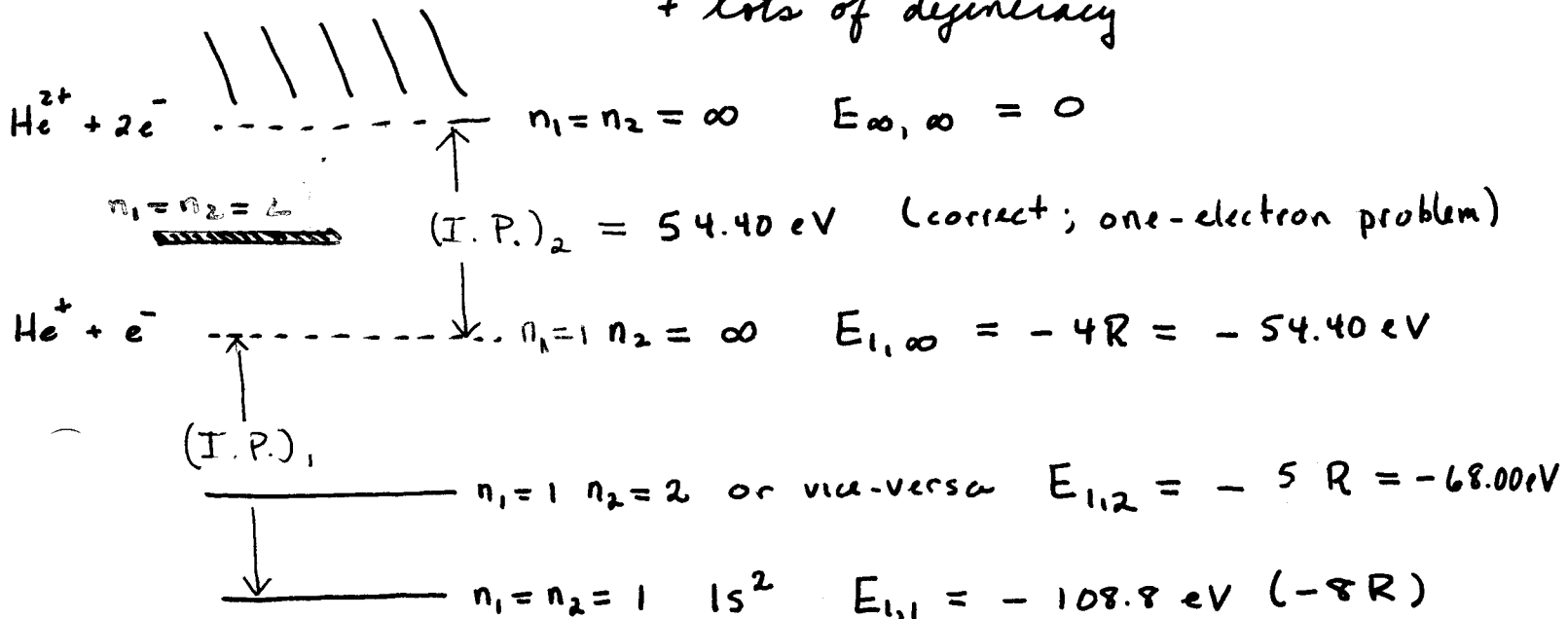
$$E = \sum_i E_i$$

↓
n_i: l_i: m_l: (s) m_s:

$$E_i = -R Z^2 / n_i^2$$

He atom Z=2 $E_{n_1, n_2} = -4R \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$

+ lots of degeneracy



(I.P.)₁^{calc} = 54.40 eV much too high since $n_1 = n_2 = 1$ level much too stable. (no e^-e^- repulsion)

(expt. value = 24.5 eV)

State embedded in continuum: consider $n_1 = n_2 = 2$ state

$$E_{2,2} = -4R \left(\frac{1}{4} + \frac{1}{4} \right) = -2R = -27.20 \text{ eV}$$

but state lies in one-electron continuum. This fact gives the state a finite width since it eventually comes apart to form $He^+ + e^-$.

Degeneracy Besides getting the energies wrong, our simple theory gets the degeneracies wrong!

Consider the lowest state $n_1 = n_2 = 1$. We know that $l_1 = l_2 = 0$, $m_{l1} = m_{l2} = 0$, so that the only degeneracy is due to spin:

$\uparrow\uparrow \quad \uparrow\downarrow \quad \downarrow\uparrow \quad \downarrow\downarrow$ $| \pm \rangle | \pm \rangle$ - a degeneracy of 4. (2×2)

But the ground state turns out to be non-degenerate!

We have so far neglected the Pauli Exclusion Principle: $|\Psi\rangle$ must be anti-symmetric to exchange of any two fermions, or symmetric to exchange of any two bosons.

identical

Electrons are fermions, so we require anti-symmetric wave functions.

$$\Psi_A = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix}$$

Slater determinant

orbital 1

orbital 2

"orbital"

set of n_2, l_2, m_{l2}, m_{s2} quantum numbers (n, l, m, s)

coordinates of electron r_2, θ_2, ϕ_2

By determinantal properties, $\Psi = \Psi_A$:

$$\Psi_A = \frac{1}{\sqrt{2}} \left(\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1) \right) \text{ exchange leads to } -\Psi_A$$

and $\Psi_A = 0$ (doesn't exist) if $\psi_1 = \psi_2$. This leads to the second formulation of the Pauli Principle:

"No two electrons can have the same four quantum numbers n, l, m_l, m_s ."

$$\psi_i = \phi_i |+\rangle \text{ or } |\phi_i |-\rangle:$$

ground state:

$$n_1 = n_2 = 1 \text{ "1s2"} \\ l_1 = l_2 = 0$$

$$\Psi_{1s^2} = \frac{1}{\sqrt{2}}$$

only non-zero combination $g=1$

$$\Psi_{1s^2} = \frac{1}{\sqrt{2}} \left[\phi_{1s}(1)\phi_{1s}(2) \right] \left[\begin{array}{cc} \uparrow & \downarrow \\ |1:+\rangle |2:-\rangle - |1:-\rangle |2:+\rangle \\ \alpha(1)\beta(2) - \beta(1)\alpha(2) \end{array} \right]$$

alternative notations: $\alpha(1)\beta(2) - \beta(1)\alpha(2)$
of spin part $|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2$

Note: one spin up, other spin down. $\uparrow\downarrow$

* Advanced note: spin state corresponds to $|S=0, M_s=0\rangle$ where S + M_s refer to total electronic spin.

1st excited state: lots of possibilities. Consider 1s2s

4 possible non-zero determinants

$$\psi_{1525} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}(1) |1: \pm\rangle & \phi_{1s}(2) |2: \pm\rangle \\ \phi_{2s}(1) |1: \pm\rangle & \phi_{2s}(2) |2: \pm\rangle \end{vmatrix}$$

$$\begin{array}{cccc} 2s & \uparrow & \downarrow & \uparrow & \downarrow \\ 1s & \uparrow & \uparrow & \downarrow & \downarrow \end{array}$$

↑
do out

can take linear combinations

Improved Energies - Manfred gets to here

If we include $H' = \sum_{i < j} \frac{e^2}{|R_i - R_j|}$ the problem becomes much more complex. One can use a variety of approximation methods:

- 1) Perturbation Theory (non-degenerate or degenerate; $1s^2 He$ done in QM class)
- 2) Variational Method
- ** 3) Central Field (Hartree-Fock) Approach

$$H = \sum_i \left[\frac{p_i^2}{2m_e} + V_c(R_i) \right] + W$$

best central approx. \rightarrow suitably chosen to minimize W

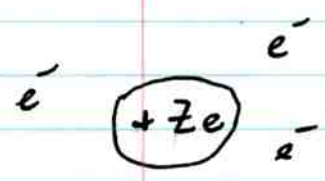
If $W=0$, $H = \sum H_i'$ and we have independent particles.

$$E = \sum_i E_i' \quad \psi = A \prod_i \phi_i(i) |i: \pm\rangle$$

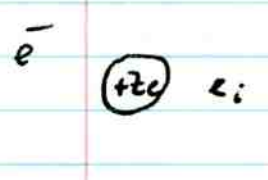
different orbitals

$V_c(R_i)$ depends on the other electrons.

Extreme Examples



$\cdot e: V_c(R_i) \rightarrow -e^2/R_i$



$V_c(R_i) \rightarrow -Ze^2/R_i$

quantum screening effect

a_i in general:

$$V_c(R_i) = -\frac{Ze^2}{R_i} + \sum_{j \neq i} e^2 \int \frac{|\phi_j(r_j)|^2 d\tau_j}{|R_i - R_j|}$$

replaces classical e^2/r_{ij}
e.g. hydrogenic

must be determined from initial guess for the wave functions of other electrons

$W=0$

wave functions $\rightarrow V_c(R_i) \rightarrow$ energies, better wave functions
 self-consistent fields

"self consistent"

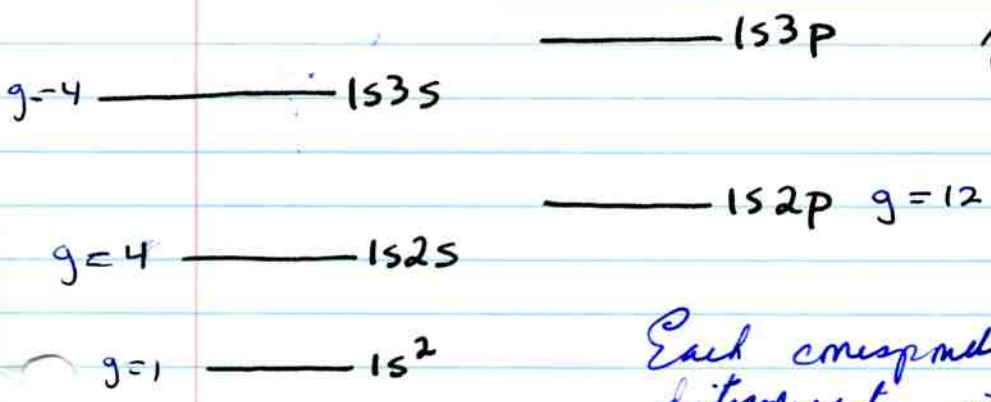
Net Result ($W=0$)

The individual m.e. electron solutions lose l degeneracy. Their energies depend on n and l. Qualitatively:

(for ≥ 2 electrons) $1s < 2s < 2p < 3s < 3p < 4s < 3d \dots$

Example: He ("configurations")

These configurations do not yet correspond to states. Remember that W is non-zero!



Each corresponds to a determinant or determinants with modified ϕ_i 's.