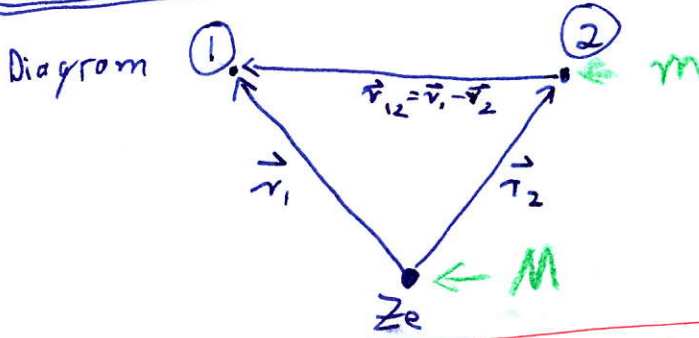


4 2.3 Two electron atoms

These include, e.g. H^- , He , Li^+
 ($z=1$), ($z=2$), ($z=3$)

Important because the ~~part~~ ^{simplest} where we see Pauli exclusion principle at work (see Eq. 1.37) and introduce essential approximation techniques. We can not solve any $2e^-$ problem ~~fully~~ exactly analytically.

2.3.1. The Schrödinger eqn for two-electron atoms



$$r_{12} = |\vec{r}_1 - \vec{r}_2|$$

$$r_i = |\vec{r}_i| \text{ etc.}$$

TISE (Eq 1.5) for Helium problem:

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\vec{r}_1}^2 - \frac{\hbar^2}{2\mu} \nabla_{\vec{r}_2}^2 - \frac{\hbar^2}{M} \nabla_{\vec{r}_1} \cdot \nabla_{\vec{r}_2} - \frac{Ze^2}{(4\pi\epsilon_0)r_1} - \frac{Ze^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} \right] \psi(\vec{r}_1, \vec{r}_2) = E \psi(\vec{r}_1, \vec{r}_2) \quad (2.23)$$

- $\mu = \frac{mM}{m+M}$ is reduced mass of electron (we used $\mu=M$ for $M \rightarrow \infty$ in chapter 1.2.3)
- Mass polarisation term $\nabla_{\vec{r}_1} \cdot \nabla_{\vec{r}_2}$ comes from separation of center of mass co-ordinate. $\rightarrow 0$ for $M \rightarrow \infty$. e_1 affects e_2 by changing reference frame.

From now on, use atomic units:

$$\hbar = 1, \quad \frac{1}{(4\pi\epsilon_0)} = 1, \quad e = 1, \quad m = 1 \quad (2.24)$$

(then hydrogen energy $E_{n,m} = -\frac{1}{2n^2}$ (see Eq. 1.19))

Hamiltonian symmetric wrt. particle inter-change operator

$$P_{12}: \vec{r}_1 | \vec{r}_2 \rightarrow \vec{r}_2 | \vec{r}_1$$

\Rightarrow Also eigenfunctions must have this symmetry [= be eigenfunction of P_{12}]

$$\psi(\vec{r}_1, \vec{r}_2) = \pm \psi(\vec{r}_2, \vec{r}_1) \quad (2.25)$$

Proof: $P_{12} \psi(\vec{r}_1, \vec{r}_2) = \lambda \psi(\vec{r}_1, \vec{r}_2)$ (is eigenfct.)
 $\stackrel{\text{also}}{=} \psi(\vec{r}_2, \vec{r}_1)$

$$P_{12}^2 \psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1, \vec{r}_2) = \lambda^2 \psi(\vec{r}_1, \vec{r}_2) \Rightarrow \lambda^2 = 1 \Rightarrow \lambda = \pm 1 \quad \square$$

There are two types of two electron states

Para states, wavefct space-symmetric $\psi_+(\vec{r}_1, \vec{r}_2) = \psi_+(\vec{r}_2, \vec{r}_1)$
Ortho states, — — — — — anti-symmetric $\psi_-(\vec{r}_1, \vec{r}_2) = -\psi_-(\vec{r}_2, \vec{r}_1)$ (2.26)

2.3.2 Spin wave functions and Pauli exclusion

• Add electron spin (is essential now, not perturbation as for Hydrogen)

• e^- are Fermions, total state must be antisymmetric under $1 \leftrightarrow 2$

• Possible spin states for two e^- $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$, where

e.g. $|\uparrow\downarrow\rangle$ is shorthand for $|\uparrow_1 = \frac{1}{2}, m_{s1} = \pm \frac{1}{2}\rangle |\downarrow_2 = \frac{1}{2}, m_{s2} = \pm \frac{1}{2}\rangle$

• Useful to move to coupled spin basis, where $\hat{S} = \hat{S}_1 + \hat{S}_2$

(see section 1.2.2)

We find:

$ S=0, m_S=0\rangle = \frac{1}{\sqrt{2}} (\uparrow\downarrow\rangle - \downarrow\uparrow\rangle)$	<u>antisymmetric</u> <u>spin singlet</u>
$ S=1, m_S=-1\rangle = \downarrow\downarrow\rangle$	<u>symmetric</u>
$ S=1, m_S=0\rangle = \frac{1}{\sqrt{2}} (\uparrow\downarrow\rangle + \downarrow\uparrow\rangle)$	<u>spin triplet</u>
$ S=1, m_S=+1\rangle = \uparrow\uparrow\rangle$	(2.27)

From Eq. (1.37) we see, allowed solutions are

$$\psi(q_1, q_2) = \psi_+(\vec{r}_1, \vec{r}_2) \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (\text{Para}) \quad (2.28)$$

$$\psi(q_1, q_2) = \psi_-(\vec{r}_1, \vec{r}_2) \times \begin{cases} |\downarrow\downarrow\rangle \\ \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\uparrow\uparrow\rangle \end{cases} \quad (\text{Ortho})$$

• Despite not appearing explicitly in Eq 2.23, spin dictates which allowed solution to pick!!!

23.3. Approximation Methods for 2 electron ^(ground state) wavefunctions

We still have to actually calculate $\Psi_{\pm}(\vec{r}_1, \vec{r}_2)$

Let's split $\hat{H}_{hel} = \hat{H}_0 + \hat{H}'$ again, where (in a.u.)

$$\hat{H}_0 = -\frac{\vec{\nabla}_{\vec{r}_1}^2}{2} - \frac{\vec{\nabla}_{\vec{r}_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} \quad \hat{H}' = \frac{1}{r_{12}} \quad (2.29)$$

Note: atomic units are nice!

We see that $\hat{H}_0 \Psi^{(0)}(\vec{r}_1, \vec{r}_2) = E^{(0)} \Psi^{(0)}(\vec{r}_1, \vec{r}_2)$ is solved

by: $\Psi^{(0)}(\vec{r}_1, \vec{r}_2) = \phi_{n\ell m}(\vec{r}_1) \phi_{n'\ell'm'}(\vec{r}_2)$ and $E^{(0)} = E_{n\ell m} + E_{n'\ell'm'}$,

with $\phi_{n\ell m}$ and $E_{n\ell m}$ given by Hydrogen solutions (1.18/1.19)

Note, that for every $E^{(0)}$, wavefunctions with $\phi_{n'\ell'm'}(\vec{r}_1) \phi_{n\ell m}(\vec{r}_2)$ are also a solution \Rightarrow exchange degeneracy

Using these:

Zero'th order approximation of Helium wavefunctions (the independent particle model)

$$\Psi_{\pm}^{(0)}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_{n\ell m}(\vec{r}_1) \phi_{n'\ell'm'}(\vec{r}_2) \pm \phi_{n'\ell'm'}(\vec{r}_1) \phi_{n\ell m}(\vec{r}_2) \right] \quad (2.30)$$

(+ = Para, - = Ortho)

• Gives ground-state energy of Helium: $E_{100,100}^{(0)} = -Z^2 \stackrel{He}{=} -4$
(Para only) \leftarrow ASK WHY?

Perturbation theory

Take into account \hat{H}' as usual (Eq. 1.26)

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

$$\text{Ground state} \int d^3r_1 \int d^3r_2 \underbrace{|\phi_{100}(r_1)|^2}_{\text{charge density @ } \vec{r}_1} \underbrace{\frac{1}{|\vec{r}_1 - \vec{r}_2|}}_{V_{int}} \underbrace{|\phi_{100}(r_2)|^2}_{\text{charge density @ } \vec{r}_2}$$

(Coulomb energy due to interaction)

$$\text{see book} \dots + \frac{5}{8} Z \quad (\text{in a.u.})$$

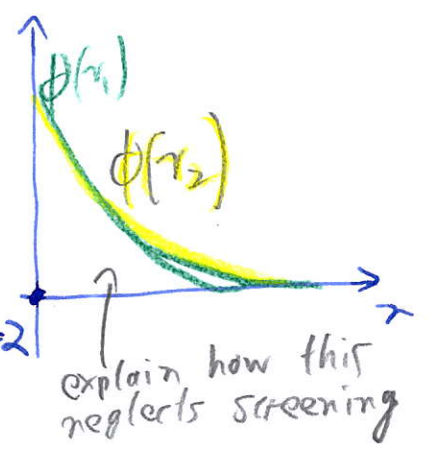
• Now we have $E^{(0)} + E^{(1)} = -Z^2 + \frac{5}{8} Z = -2.75$ (getting better) (exact! -2.904) | 28

(Variational huge trial fct)

Variational Method

Look at $\psi_+^{(0)}(r_1, r_2) = \phi_{100}(\vec{r}_1) \phi_{100}(\vec{r}_2)$ (2.31)

$$\phi_{100}(\vec{r}_1) \stackrel{\text{a.u.}}{\text{Eq. (1.18)}} \sqrt{\frac{Z^3}{\pi}} \exp[-Zr]$$



Now try to improve on this by introducing $Z \rightarrow Z_e$
 a screened charge $Z_e \rightarrow Z_e$
 (effective)

Determine Z_e from variational principle

~~Not determined to determine Z_e use trial function~~

Variational Principle

- Energy functional $E[\phi] = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$ is extremal (2.32)
- at an eigenstate of \hat{H} : $\delta E[\psi_n] = 0$
- The groundstate energy $E_0 \leq E[\phi]$ for any ϕ

• δE is a functional derivative of variation of the energy functional: "how does E change for any variation of ϕ (around ψ_n)"

$$\delta E \langle \phi | \phi \rangle + E \langle \delta \phi | \phi \rangle + E \langle \phi | \delta \phi \rangle = \langle \delta \phi | \hat{H} | \phi \rangle + \langle \phi | \hat{H} | \delta \phi \rangle$$

• Related to functional derivative $\frac{\delta E}{\delta \phi(x)}$ (see books)

• A special variation is $\delta E = \frac{\partial E}{\partial Z_e} \delta Z_e \stackrel{!}{=} 0$

To find $\frac{\partial E}{\partial Z_e}$, we insert (2.31) with $Z \rightarrow Z_e$ into (2.32)

$$E[\psi_+^{(0)}] = \underbrace{\langle \psi_+^{(0)} | \hat{T}_1 + \hat{T}_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} | \psi_+^{(0)} \rangle}_{\text{see assignment 1}} = Z_e^2 \underbrace{- 2Z_e}_{\text{from } \hat{H}} + \frac{5}{8} Z_e \underbrace{\text{from trial fun}}$$

$\frac{\partial E}{\partial Z_e} = 0 \iff Z_e = Z - \frac{5}{16}$ (effective charge reduced, as expected)

• Now ground-state energy of Helium $E[\psi_+^{(0)}] = -\left(Z - \frac{5}{16}\right)^2$ a.u. = -2.848 a.u. (even closer to "exact" -2.904)

Screening in central field approximation

Going back to independent particle model / 0'th order PT,
 we can rewrite Hamiltonians:

$$\hat{H}_0 \quad \hat{H}_1$$

$$-\frac{\nabla_{r_1}^2}{2} - \frac{\nabla_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} \quad \frac{1}{r_{12}}$$

↓ (just change / rewrite \hat{H}_0)

$$-\frac{\nabla_{r_1}^2}{2} - \frac{\nabla_{r_2}^2}{2} + V(r_1) + V(r_2) \quad \frac{1}{r_{12}} - \frac{Z}{r_1} - V(r_1) - \frac{Z}{r_2} - V(r_2)$$

See that if we choose the central field $V(r) = -\frac{Z-S}{r} = -\frac{Z_e}{r}$ (2.33)

with $Z_e = Z - \frac{S}{10}$ we obtain exactly our variational solution as eigenstates in 0'th order PT. The re-writing has effectively made \hat{H}_1 "smaller". S is the screening factor ($S = \frac{S}{10} = 0.31$ for He)

• Central field concept will be even more useful for $N \gg 2$ electrons

2.3.4. Excited states of two-electron atoms

Much of 2.3.3 can be generalized to excited states.

Let us consider perturbation theory of:

$$\Psi_{\pm}^{(0)}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_{1,00}(\vec{r}_1) \phi_{n,l,m}(\vec{r}_2) \pm \phi_{n,l,m}(\vec{r}_1) \phi_{1,00}(\vec{r}_2) \right] \quad (2.34)$$

$$E^{(0)} = E_{1,00} + E_{n,l,m} \quad \text{with } \text{correlation}$$

First order excited state interaction energy
 \pm Para, $-$ Ortho, (Ortho not possible for ground-state) (2.35)

$$E_{\pm}^{(1)} = J \pm K \quad \text{with}$$

$$J = \int d^3r_1 d^3r_2 |\phi_{1,00}(r_1)|^2 \frac{1}{r_{12}} |\phi_{n,l,m}(r_2)|^2 \quad \text{Coulomb (direct) integral}$$

$$K = \int d^3r_1 d^3r_2 \phi_{1,00}^*(r_1) \phi_{n,l,m}^*(r_2) \frac{1}{r_{12}} \phi_{1,00}(r_2) \phi_{n,l,m}(r_1) \quad \text{exchange integral}$$

• Using $\vec{S}_1 \cdot \vec{S}_2 = \frac{1}{2} S^2 - \frac{3}{4}$ can rewrite:

$$E_{\pm}^{(1)} = J - \frac{1}{2} (1 + 4 \vec{S}_1 \cdot \vec{S}_2) K \Rightarrow \text{spin dependence of energy}$$

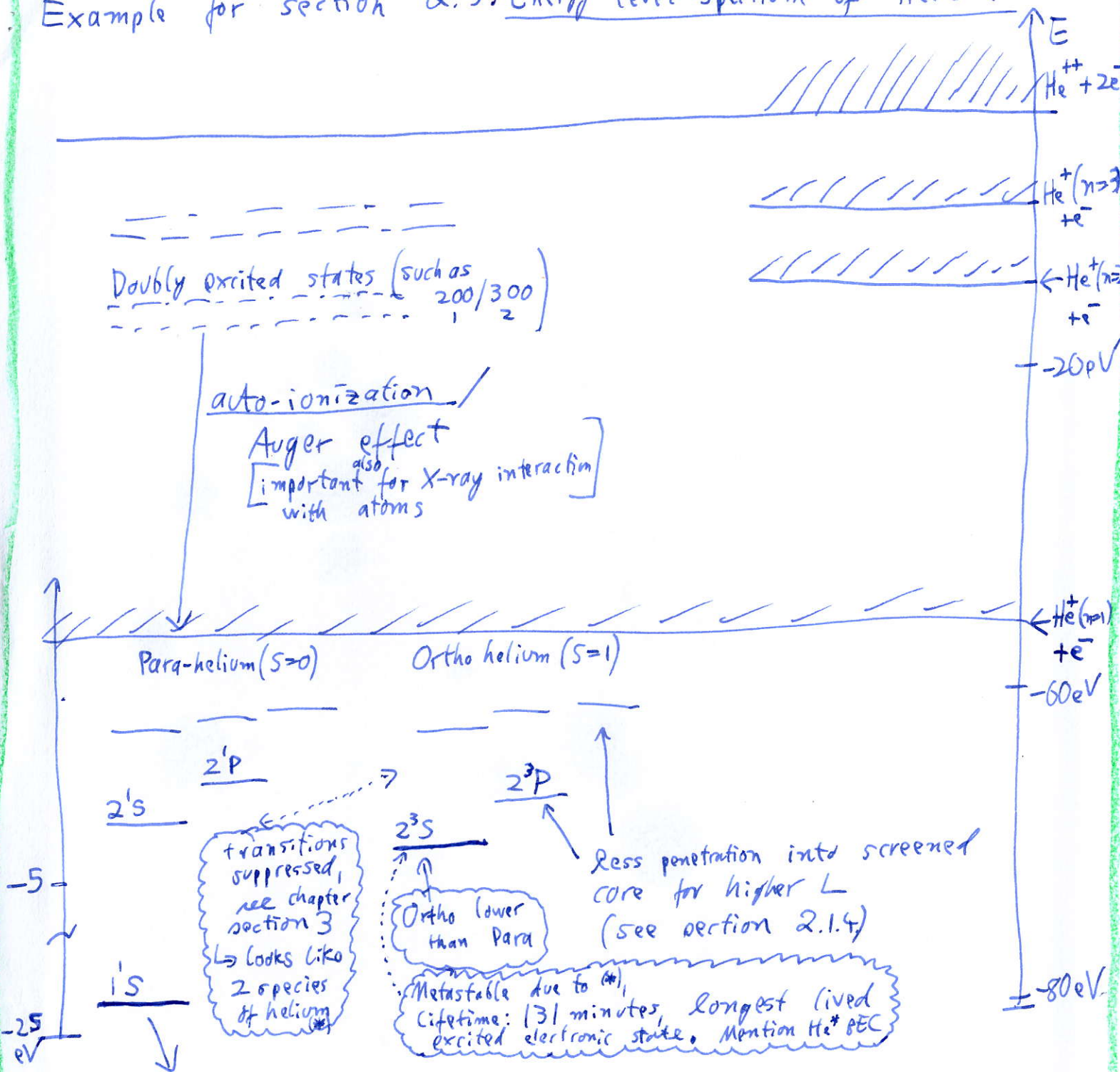
ME of perturbation between the two different states of superposition. "Swap amplitude"

• See $J > 0$. Turns out J, K depend on n, l only

• usually also $K > 0 \Rightarrow$ Ortho ($S=1$) has lower energy

$$J \rightarrow J_{nl} \quad K \rightarrow K_{nl}$$

Example for section 2.3: Energy level spectrum of Helium



Helium groundstate, ionization potential

theory (full): $24.586812487292\text{ eV} \pm 6 \cdot 10^{-6}\text{ eV}$

expt. : $24.5866274689038\text{ eV} \pm 1.8 \cdot 10^{-5}\text{ eV}$

(QM seems to work)