Week 4

PHY 402 Atomic and Molecular Physics
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2.3 Two Electron Atoms

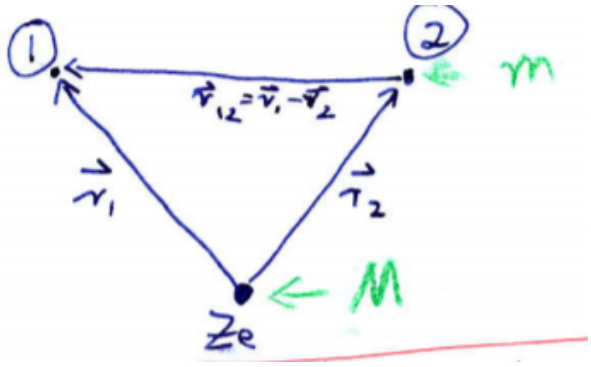
These include , e.g., $\underbrace{H^-}_{Z=1}$, $\underbrace{He}_{Z=2}$, $\underbrace{Li^+}_{Z=3}$

Important because they are the simplest atoms where we see the Pauli Exclusion Principle at work (see Eq. (1.62)) and can introduce essential approximation techniques. We cannot solve any two e^- problems exactly analytically.

2.3.1 The Schrödinger Equation for two-electron atoms

We need co-ordinates for both electrons now, see diagram below.

$$r_{12} = |\mathbf{r_1} - \mathbf{r_2}| \tag{2.64}$$
$$r_1 = |\mathbf{r_1}| \tag{2.65}$$



In terms of these we write the

TISE (see Eq. (1.7)) for the Helium problem

$$\underbrace{\left[-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}_{r_1}^2-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}_{r_2}^2-\frac{\hbar^2}{M}\boldsymbol{\nabla}_{r_1}\cdot\boldsymbol{\nabla}_{r_2}-\frac{Ze^2}{(4\pi\epsilon_0)\,r_1}-\frac{Ze^2}{(4\pi\epsilon_0)\,r_2}+\frac{e^2}{(4\pi\epsilon_0)\,r_{12}}\right]}_{\equiv\hat{H}_{hel}}\psi\left(\mathbf{r_1},\mathbf{r_2}\right)$$
$$=E\psi\left(\mathbf{r}_1,\mathbf{r}_2\right) \tag{2.66}$$

- $\mu=\frac{m_eM}{m_e+M}$ is reduced mass of the electron, m_e electron mass, M nuclear mass. (We used $\mu=m_e$ for $M\to\infty$ in section 1.2.3)
- Mass polarisation term $\boldsymbol{\nabla}_{r_1}\cdot\boldsymbol{\nabla}_{r_2}$ comes from separation of centre of mass coordinate. It vanishes for $M\to\infty$.

From now on, use atomic units:

$$\hbar=1 \qquad \frac{1}{4\pi\epsilon_0}=1 \qquad e=1 \qquad \underbrace{m}_{\text{electron mass}}=1 \tag{2.67}$$

(then hydrogen energy $E_{nlm}=-\frac{1}{2n^2}$(see Eq. (1.43)) and $a_0=1$)

- The Hamiltonian is symmetric with respect to particle **position** interchange operator

$$P_{12}:\mathbf{r_1}|\mathbf{r_2}\longrightarrow\mathbf{r_2}|\mathbf{r_1} \tag{2.68}$$

  $\Rightarrow$ Also eigen-functions must have this symmetry [=be eigenfunction of P_{12}]

$$\Rightarrow\psi\left(\mathbf{r_1},\mathbf{r_2}\right)=\pm\psi\left(\mathbf{r_2},\mathbf{r_1}\right) \tag{2.69}$$

- Note, this is not the same as the complete particle exchange operation used in writing Bose/Fermi symmetries Eq. (1.62), where we have to swap all properties, not just position.

There are two types of two electron states
Para States, wave functions spatially symmetric:

$$\psi_+\left(\mathbf{r_1},\mathbf{r_2}\right)=\psi_+\left(\mathbf{r_2},\mathbf{r_1}\right) \tag{2.70}$$

Ortho States, wave functions spatially anti-symmetric:

$$\psi_-\left(\mathbf{r_1},\mathbf{r_2}\right)=\psi_-\left(\mathbf{r_2},\mathbf{r_1}\right) \tag{2.71}$$

2.3.2 Spin Wave functions and Pauli Exclusion Principle

- Now we add electron spin into the picture, it becomes essential now, not jut a small perturbation as for Hydrogen.
- e^- are fermions, total state must be anti-symmetric under 1⇔2
- Possible spin states for two electrons are: $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$, see section 1.2.2.
- Useful to move to coupled spin basis, where $\hat{S} = \hat{s_1} + \hat{s_2}$, see also section 1.2.2.

We find

Spin pair states

$$|S=0, m_S=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \qquad \frac{\text{Anti-symmetric}}{\text{spin singlet}} \qquad (2.72)$$

$$|S=1, m_S=-1\rangle = |\downarrow\downarrow\rangle \qquad \text{Symmetric} \qquad (2.73)$$

$$|S=1, m_S=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \qquad \text{spin triplet} \qquad (2.74)$$

$$|S=1, m_S=1\rangle = |\uparrow\uparrow\rangle \qquad (2.75)$$

Solutions to the helium problem have to satisfy Eq. (2.70)-(2.71) (spatial symmetry) and Eq. (1.62) (total fermionic symmetry). Thus all allowed solutions can be written as

$$\psi(q_1, q_2) = \psi_+(\mathbf{r_1}, \mathbf{r_2}) \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \qquad \text{(Para)} \qquad (2.76)$$

$$\psi(q_1, q_2) = \psi_-(\mathbf{r_1}, \mathbf{r_2}) \begin{cases} |\downarrow\downarrow\rangle \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \\ |\uparrow\uparrow\rangle \end{cases} \qquad \text{(Ortho)} \qquad (2.77)$$

- Despite not actually appearing explicitly in the Hamiltonian of (2.66), the total spin dictates which spatial symmetry the solution must have!

2.3.3 Approximate methods for 2 electron groundstate wavefunction

So far we only classified solutions according to spin and spatial symmetry, we yet have to actually determine the symmetric and anti-symmetric eigen functions $\psi_\pm(\mathbf{r_1}, \mathbf{r_2})$
Lets split $\hat{H}_{hel} = \hat{H}_0 + \hat{H}'$ again, where (in atomic units, abbreviated a.u.)

$$\hat{H}_0 = -\frac{\boldsymbol{\nabla}_{r_1}^2}{2} - \frac{\boldsymbol{\nabla}_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} \qquad \hat{H}' = \frac{1}{r_{12}} \qquad (2.78)$$

Note: Atomic units save a lot of writing!
We see that the unperturbed eigen-problem $\hat{H}_0\psi^{(0)}(\mathbf{r_1},\mathbf{r_2}) = E^{(0)}\psi^{(0)}(\mathbf{r_1},\mathbf{r_2})$ is solved by the product Ansatz:

$$\psi^{(0)}(\mathbf{r_1},\mathbf{r_2}) = \phi_{nlm}(\mathbf{r_1})\,\phi_{n'l'm'}(\mathbf{r_2}), \tag{2.79}$$

$$E^{(0)} = E_{nlm} + E_{n'l'm'}, \tag{2.80}$$

with ϕ_{nlm} and E_{nlm} given by Hydrogen solutions ((1.35) and (1.43)).

- Note, that for every energy $E^{(0)}$, the wavefunctions with swapped indices: $\phi_{n'l'm'}(\mathbf{r_1})\,\phi_{nlm}(\mathbf{r_2})$ are an equally valid solution. This is called ⇒ exchange degeneracy.
- This allows us now to construct solutions satisfying Eq. (2.70)-(2.71), namely

Zero'th order approximation for Helium wavefunctions
This is also called independent particle model

$$\psi^{(0)}_{\pm}(\mathbf{r_1},\mathbf{r_2}) = \frac{1}{\sqrt{2}}\left[\phi_{nlm}(\mathbf{r_1})\,\phi_{n'l'm'}(\mathbf{r_2}) \pm \phi_{n'l'm'}(\mathbf{r_1})\,\phi_{nlm}(\mathbf{r_2})\right] \tag{2.81}$$

Where $+$ =Para, and $-$ =Ortho. Only for Para states $\{n',l',m'\} = \{n,l,m\}$ is possible, then $\psi^{(0)}_{+}(\mathbf{r_1},\mathbf{r_2}) = \phi_{nlm}(\mathbf{r_1})\,\phi_{nlm}(\mathbf{r_2})$.

- Gives ground-state energy of $\underbrace{\text{Helium}}_{\text{(Para only)}}$: $E^{(0)}_{100,100} = -\frac{Z^2}{2}\left(\frac{1}{1^2}+\frac{1}{1^2}\right) = -Z^2 \overset{\text{He}}{=} -4$

So far we have completely ignored electron-electron interactions in $\hat{H}'$, let's rectify this now: PerturbationTheory

Take into account $\hat{H}'$ as in Eq. (1.50), focussing on the ground-state only for now:

$$E^{(1)} = \langle\psi^{(0)}_{\pm}|\hat{H}'|\psi^{(0)}_{\pm}\rangle \tag{2.82}$$

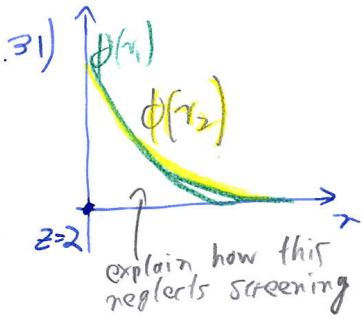
$$\overset{\text{Ground state}}{=} \int d^3r_1 \int d^3r_2 \quad \underbrace{|\phi_{100}(r_1)|^2}_{\text{Charge density at } \mathbf{r}_1} \quad \frac{1}{|r_1-r_2|} \quad \underbrace{|\phi_{100}(r_2)|^2}_{\text{Charge density at } \mathbf{r}_2} \tag{2.83}$$

$$\overset{\text{See Book}}{=} \ldots\ldots + \frac{5}{8}Z \qquad \text{in a.u.} \tag{2.84}$$

In the second line above we recognize the electro-static interaction energy of the charge densities due to electron 1 and 2.

- Now we have $E^{(0)} + E^{(1)} = -Z^2 + \frac{5}{8}Z = \underbrace{-2.75}_{\text{getting better}}$ ("exact" -2.904)

Variational Method



left: Sketch of helium electron wave-functions with (yellow) and without screening (green).
Look at

$$\psi_{+}^{(0)}\left(\mathbf{r}_1,\mathbf{r}_2\right)=\phi_{100}\left(\mathbf{r_1}\right)\phi_{100}\left(\mathbf{r_2}\right), \tag{2.85}$$

$$\phi_{100}\left(\mathbf{r_1}\right)\underset{\text{Eq. (1.35)}}{\overset{\text{a.u.}}{=}}\sqrt{\frac{Z^3}{\pi}}\exp^{[-Zr_1]} \tag{2.86}$$

Now try to improve on this by introducing a screened (or effective) charge $Z\to Z_{\text{eff}}$. Let us take the trial state

$$\psi^{(0)}{}_{\text{trial}}\left(\mathbf{r}_1,\mathbf{r}_2\right)=\phi_{\text{trial}}(\mathbf{r}_1)\phi_{\text{trial}}(\mathbf{r}_2)$$

$$\phi_{\text{trial}}(\mathbf{r})=\sqrt{\frac{Z_{\text{eff}}^3}{\pi}}\exp^{[-Z_{\text{eff}}r]}, \tag{2.87}$$

as guess for the two-electron wave function. We have to find the "best" value of Z_{eff} from variational principle

Variational Principle

- Energy functional

$$E\left[\phi\right]=\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \tag{2.88}$$

  is extremal at an eigenstate ψ_n of $\hat{H}$, that means

$$\delta E\left[\psi_n\right]=0. \tag{2.89}$$

- The groundstate energy $E_0\le E\left[\phi\right]$ for any trial state ϕ. Thus the minimal energy we can reach by changing the parameters in our trial state, will be closest to the true ground-state energy.

Variational derivatives:

- δE is a variation of the energy functional: Multiply Eq. (2.88) by $\langle\phi|\phi\rangle$ and take the total derivative wrt. the state

$$\delta E\langle\phi|\phi\rangle + E\langle\delta\phi|\phi\rangle + E\langle\phi|\delta\phi\rangle = \langle\phi|\hat{H}|\delta\phi\rangle + \langle\delta\phi|\hat{H}|\phi\rangle \tag{2.90}$$

(*"How does the energy $E[\phi]$ change for a small variation $\phi + \delta\phi$ around ϕ?"*)

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

- A special variation is $\delta E = \frac{\partial E}{\partial Z_{\text{eff}}}\delta Z_{\text{eff}} \stackrel{!}{=} 0$

To find $\frac{\partial E}{\partial Z_{\text{eff}}}$, we insert Eq. (2.87) into the energy functional Eq. (2.88):

$$E\left[\psi^{(0)}{}_{\text{trial}}\right] = \langle\psi^{(0)}{}_{\text{trial}}| \underbrace{\hat{T}_1 + \hat{T}_2 - \frac{Z}{r_1} - \frac{Z}{r_2}}_{\text{see QM1/ standard methods}} + \frac{1}{r_{12}}|\psi^{(0)}{}_{\text{trial}}\rangle = Z_{\text{eff}}^2 - 2ZZ_{\text{eff}} + \frac{5}{8}Z_{\text{eff}}. \tag{2.91}$$

- The term involving $1/r_{12}$ gives rise to the same integral as in the perturbation theory segment one page above.
- In the expression above, factors Z stem from the Hamiltonian, but factors of Z_{eff} from the trial function.
- $$\frac{\partial E}{\partial Z_{\text{eff}}} = 0 \Leftrightarrow Z_{\text{eff}} = Z - \frac{5}{16} \qquad \text{effective charge reduced, as expected} \tag{2.92}$$
- Now ground state energy of Helium $E\left[\phi_{\text{trial}}\right] = -\left(Z - \frac{5}{16}\right)^2$a.u.= -2.848 a.u. (even closer to "exact" -2.904)

Screening in the Central Field approximation

Going back to independent particle model/ 0'th order P.T, we can rewrite Hamiltonians as indicated by the vertical arrow below:

$\hat{H}_0$	$\hat{H}'$
$-\frac{\boldsymbol{\nabla}_{r_1}^2}{2} - \frac{\boldsymbol{\nabla}_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2}$	$\frac{1}{r_{12}}$
$\Downarrow$	
$-\frac{\boldsymbol{\nabla}_{r_1}^2}{2} - \frac{\boldsymbol{\nabla}_{r_2}^2}{2} + V(r_1) + V(r_2)$	$\frac{1}{r_{12}} - V(r_1) - V(r_2) - \frac{Z}{r_1} - \frac{Z}{r_2}$

(2.93)

This just constitutes a re-allocation of what we call $\hat{H}_0$ and what we call $\hat{H}'$.

See that if we choose the **central field** below for our potential energy,

$$V(r) = -\frac{Z-S}{r} = -\frac{Z_{\text{eff}}}{r} \tag{2.94}$$

with $Z_{\text{eff}} = Z - \frac{5}{16}$ we obtain variational solution as eigenstates in 0'th order PT.[2]

The re-writing has effectively made $\hat{H}'$ "smaller". S is the screening factor. ($S = \frac{5}{16} = 0.31$ for He)

- This central field concept will be even more useful for $N > 2$ electrons.

2.3.4 Excited States of Two electron atoms

Much of section 2.3.3 can be generalised to excited states.
Let us consider perturbation theory of:

$$\psi_{\pm}^{(0)}(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{\sqrt{2}} \left[\phi_{100}(\mathbf{r_1})\,\phi_{nlm}(\mathbf{r_2}) \pm \phi_{nlm}(\mathbf{r_1})\,\phi_{100}(\mathbf{r_2})\right] \tag{2.95}$$

The unperturbed energy is $E^{(0)} = E_{nlm} + E_{100}$. For the perturbed results we find:

First Order excited state with interaction energy

$$E_{\pm}^{(1)} = J \pm K \qquad + = \text{para}, - = \text{ortho, (ortho not possible for ground state)} \tag{2.96}$$

$$J = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2\, |\phi_{100}(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\phi_{nlm}(\mathbf{r}_2)|^2 \qquad \text{Coulomb (direct) integral} \tag{2.97}$$

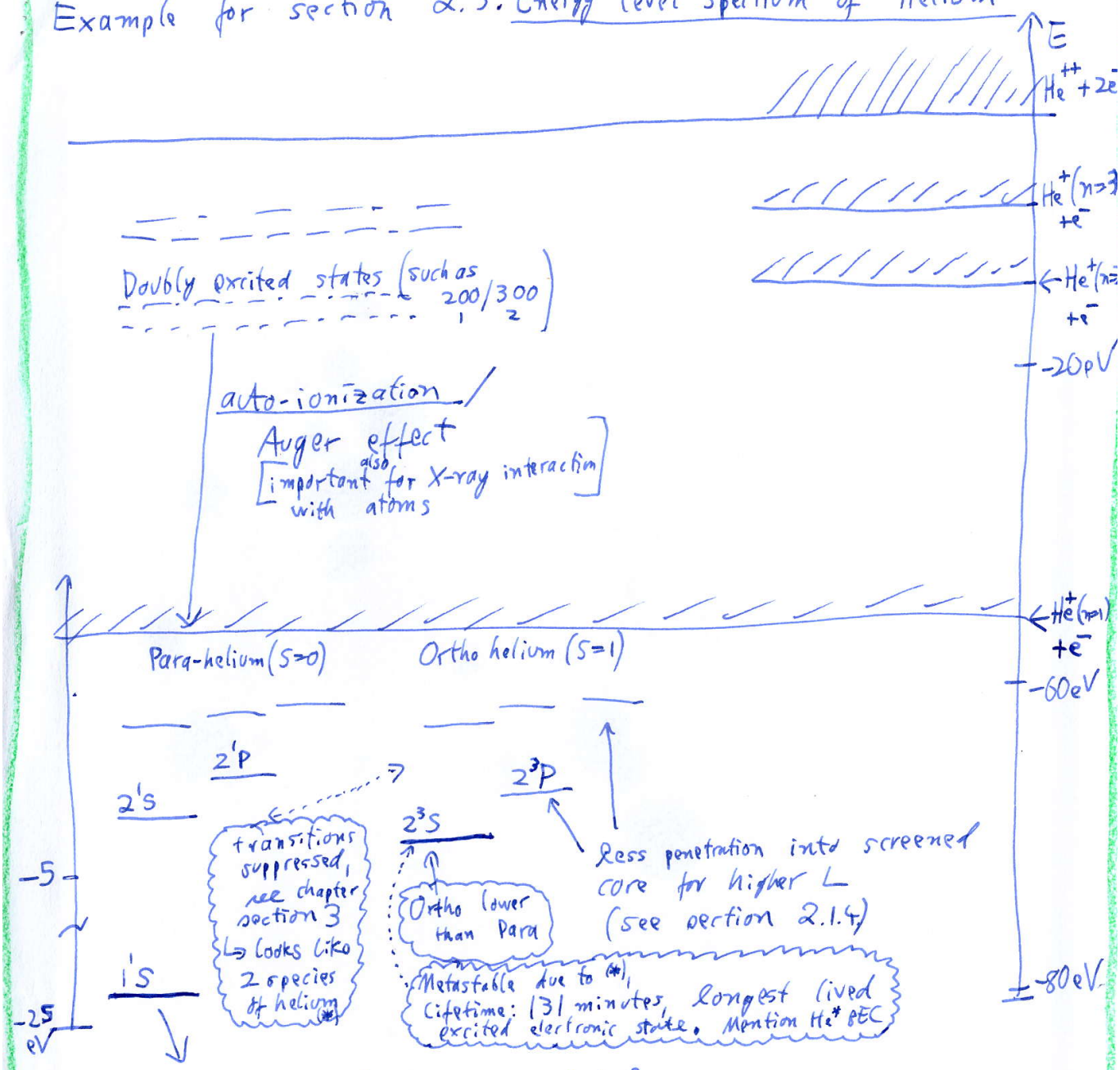
$$K = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2\, \phi_{100}^*(\mathbf{r}_1)\phi_{nlm}^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{100}(\mathbf{r}_2)\phi_{nlm}(\mathbf{r}_1) \quad \text{Exchange integral} \tag{2.98}$$

- Using $\hat{\boldsymbol{S}}_{\mathbf{1}} \cdot \hat{\boldsymbol{S}}_{\mathbf{2}} = \frac{1}{2}\hat{\boldsymbol{S}}^{\mathbf{2}} - \frac{3}{4}$, we can express the energies as
  $E_{\pm}^{(1)} = J - \frac{1}{2}\left(1 + 4\hat{\boldsymbol{S}}_{\mathbf{1}} \cdot \hat{\boldsymbol{S}}_{\mathbf{2}}\right) K \Rightarrow$ spin dependence of energy. Note that the energy became spin dependent because of the required allocation (2.76)-(2.77) of spatial symmetry to total electron spin.
- When evaluating integrals we find that $J > 0$ (*see BJ book).* It also turns out that J, K depend on n, l, hence ($J \to J_{nl}$, $K \to K_{nl}$).
- Usually also $K > 0 \Rightarrow$ Thus the ortho state ($S = 1$) has a lower energy.

All that we have learnt so far (and some more) enters the energy level diagram of helium on the next page:

[2] Finding eigenstates of the newly arranged $\hat{H}_0$ in (2.93) proceeds as we did for finding Eq. (2.81), except in the solution we have to replace everywhere $Z \to Z_{\text{eff}}$. Thus we obtain the solution (2.87).

Example for section 2.3: Energy level spectrum of Helium



Helium groundstate, ionization potential

including finestructure etc...

theory (fdC): 24.58661248 7292 eV ± $6 \cdot 10^{-6}$ eV

expt. : 24.58 66 27 468 90 38 eV ± $1.8 \cdot 10^{-5}$ eV

(QM seems to work)