

Week 5

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.

2.4 Many-electron atoms

- Already cannot solve the two electron problem exactly. The variational approach also becomes too hard for large numbers of electrons. Now, the central field approximation will be very useful.

Many-electron (N) Schrödinger equation:

$$\hat{H}\psi(q_1, q_2, \dots, q_N) = E\psi(q_1, q_2, \dots, q_N)$$

$$q_k = \{m_{sk}, \mathbf{r}_k\} \text{ (spin and position variables)}$$

$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} \right) + \sum_{i < j=1}^N \frac{1}{r_{ij}} \text{ (in atomic units)} \quad (2.99)$$

- Eq. (2.4) constitutes a PDE, for a wavefunction with $3N$ spatial plus 2^N discrete co-ordinates \implies very impossible to solve directly.
- This problem generically arises in quantum-many-body-physics.
- Unlike two electron case, $\hat{H}' = \sum_{i < j=1}^N 1/r_{ij}$ generally is not small due to many terms in the sum.

2.4.1 Central field approximation

Now the independent-particle model and central field approximation become indispensable:



left: When considering a selected electron, the most important effect of other $(N - 1)$ electrons is collectively screening the nuclear charge, which however still leaves the potential for the N th electron spherically symmetric (to a good approximation).

Similar to our treatment of Helium, we write for this radial potential felt by electron number i

$$V(\mathbf{r}_i) = -\frac{Z}{|\mathbf{r}_i|} + S(|\mathbf{r}_i|) \quad (\text{Now screening is } r\text{-dependent}). \quad (2.100)$$

We now re-write Eq.(2.99), ignoring spin for now

$$\hat{H}_c = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V(\mathbf{r}_i) \right) = \sum_{i=1}^N \hat{h}_i \quad (2.101)$$

$$\hat{H}' = \sum_{i < j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z}{r_i} + V(\mathbf{r}_i) \right) = \sum_{i < j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N S(\mathbf{r}_i) \quad (2.102)$$

such that $\hat{H} = \hat{H}_c + \hat{H}'$ (just re-writing).

- \hat{H}_c is central field Hamiltonian.
- Expect eigenfunctions of \hat{H}_c to be better than those of $\hat{H}_0 = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 - Z/r_i \right)$.
- Challenge is to find out suitable $S(\mathbf{r}_i)$ or $V(\mathbf{r}_i)$.

Central field Schrödinger equation

$$\hat{H}_c \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_c \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (2.103)$$

can be solved using

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = u_{a_1}(\mathbf{r}_1) u_{a_2}(\mathbf{r}_2) \dots u_{a_N}(\mathbf{r}_N); \quad a_i \equiv \{n_i l_i m_i\} \quad (2.104)$$

where,

$$\left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V(\mathbf{r}_i) \right) u_{a_i}(\mathbf{r}_i) = E_i u_{a_i}(\mathbf{r}_i), \quad E_c = \sum_i E_i. \quad (2.105)$$

The functions $u_{n_i m_i l_i}(\mathbf{r}_i)$ are called central-field orbitals.

- Exercise: Show directly that (2.104) is a solution for (2.103).

- To actually find the central field orbitals, as for hydrogen states, we write $u_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$ with Y_{lm} exact same as for H (spherical harmonics), but R_{nl} determined from the radial equation:

$$-\frac{1}{2} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R_{nl}(r) + \underbrace{V(r)}_{\neq} R_{nl}(r) = E_{nl} R_{nl}(r). \quad (2.106)$$

potential used for Hydrogen
due to screening

- Now we can use the following iterative procedure:
 - (i) Solve (2.106) with some *trial* $V(\mathbf{r}_i)$ to determine the $u_{a_i}(\mathbf{r}_i)$.
 - (ii) Use the obtained $u_{a_i}(\mathbf{r}_i)$ to infer the electron charge distributions.
 - (iii) Use the charge distribution to infer the screened potential $V(\mathbf{r}_i)$ with usual electro-statics methods.
 - (iv) Loop back to step (i) using the updated screened potential $V(\mathbf{r}_i)$.
 - (v) Repeat iteration until nothing changes any more.
- We will see one method that formalises this later.
- However we can learn a lot without doing the actual iteration, from two known limits:

$$V(r) \rightarrow -\frac{Z}{r} \quad (\text{for } r \mapsto 0), \quad (2.107)$$

here the electron is closer to the nucleus than all others, so no screening can take place, and

$$V(r) \rightarrow -\frac{Z - (N - 1)}{r} \quad (\text{for } r \mapsto \infty), \quad (2.108)$$

here all $N - 1$ other electrons are closer to the nucleus and screen its charge as much as possible.

2.4.2 Spin and Pauli-exclusion principle

- Product states $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = u_{a_1}(\mathbf{r}_1) \dots u_{a_N}(\mathbf{r}_N)$ do not in general satisfy the anti-symmetry requirements of Eq. (1.62) for fermions, and we have not yet included spin ($\mathbf{r}_N \rightarrow q_N$, see Eq.(2.99)).

Introduce spin-orbitals:

$$\begin{aligned} \underbrace{u_{nlm_l m_s}(q)}_{\equiv \alpha} &= u_{nlm_l}(\mathbf{r}) |\chi\rangle_{m_s} \\ &= R_{nl}(r) Y(\theta, \phi) |\chi\rangle_{m_s} \end{aligned} \quad (2.109)$$

with

$$|\chi\rangle_{+\frac{1}{2}} = |\uparrow\rangle, \quad |\chi\rangle_{-\frac{1}{2}} = |\downarrow\rangle.$$

In terms of these, a valid fermionic N -electron total wavefunction is given by a Slater-determinant

$$\psi_c(q_1, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \cdots & u_\nu(q_1) \\ u_\alpha(q_2) & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ u_\alpha(q_N) & \cdots & \cdots & u_\nu(q_N) \end{vmatrix} \quad (2.110)$$

Reminder: For matrix $A = \{a_{ij}\}$, the determinant $\det A = |A| = \sum_{\sigma \in S_N} \text{sgn}(\sigma) \prod_{i=1}^N a_{i\sigma_i}$.
Permutations

- We see that this enforces antisymmetry, since determinant changes sign when we exchange two rows (*math course*).
- Also, if for any indices $\alpha = \beta \implies \det = 0$. (Since, it also changes sign if we exchange two columns. This means there can never be two electrons in the same spin-orbital.)
- Set of electron quantum numbers $[\alpha, \beta, \dots, \nu]$ in (2.110) is called electron-configuration.
- Let us define also

the <u>total angular momentum</u> of all electrons	$\mathbf{J}_{tot} = \sum_{i=1}^N \mathbf{J}_i$
the <u>total orbital angular momentum</u> of electrons	$\mathbf{L}_{tot} = \sum_{i=1}^N \mathbf{L}_i$
the <u>total spin</u> of electrons	$\mathbf{S}_{tot} = \sum_{i=1}^N \mathbf{S}_i$

(2.111)

- Note that $[\hat{H}_c, \mathbf{L}_{tot}] = 0$, $[\hat{H}_c, \hat{\mathbf{S}}_{tot}] = 0$ for the central field Hamiltonian \hat{H}_c in Eq.(2.101).

\implies We can in principle write all many electron eigenstates also as eigenstates of \hat{L}_{tot} , \hat{S}_{tot} . However, note, the the Slater determinant (2.110) is not yet in general an eigenstate of \hat{L}_{tot} , \hat{S}_{tot} .

Atomic terms A state of multi-electron atoms with well defined quantum numbers for the total angular momenta J for \mathbf{J}_{tot} , L for \mathbf{L}_{tot} and S for \mathbf{S}_{tot} is called term, denoted with a term symbol

$$^{2S+1}L_J, \quad (2.112)$$

c.f. Example p. 24.

2.4.3 Ground state energetic ordering and periodic table

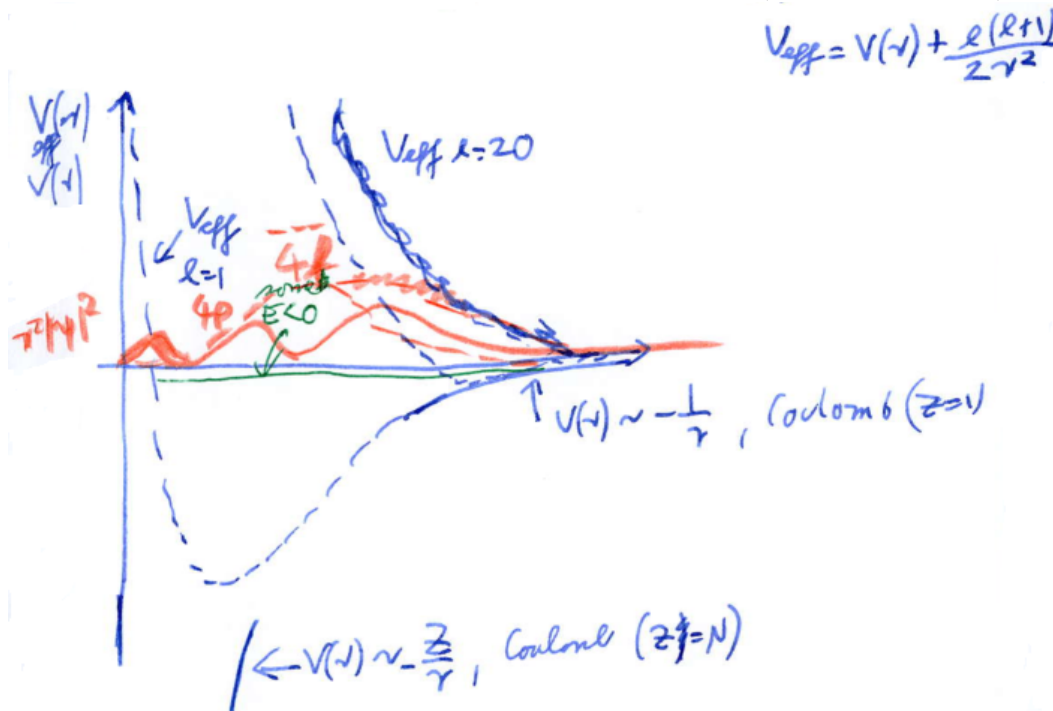
- So far we have not really solved the many-electron-atom problem since we did not yet calculate $S(\mathbf{r})$. But, most essential properties of all atoms, incorporated into the periodic table, can be understood already now, based on some $V(\mathbf{r})$ with properties (2.107)-(2.108).

Angular momentum versus screening ($N = Z$ atoms):

Revisit Eq.(2.106):

$$-\frac{1}{2} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R_{nl}(r) + \underline{V(r)} R_{nl}(r) = E_{nl} R_{nl}(r). \quad (2.113)$$

We can again combine the underlined pieces into an effective potential $V_{\text{eff}} = V(r) + \frac{l(l+1)}{2r^2}$ that includes the centrifugal barrier due to angular momentum (as in section 1.2.3).



- The centrifugal potential $l(l+1)/2r^2$ pushes the wavefunction further out (to larger r), the higher the value of l .
- All higher l -states thus feel the unscreened and stronger $-Z/r$ potential less than lower l states thus energy typically increases with l .
- Energy E_i in Eq.(2.105) depends on n, l of all electrons (but not their m_l, m_s while we ignore fine and hyperfine structure).
 \implies electrons with the same n, l are said to belong to the same sub-shell and are also called equivalent electrons.

- For a given selection of the two numbers (n, l) , there are $2(2l + 1)$ equivalent electrons (size of shell).
- To build the periodic table, we fill shells starting from low energies.

See table 8.3, Fig 8.1 of the book BJ, also follow <https://ptable.com/>

- $4s$ states fill before $3d$ (because $3d$ has so much centrifugal potential) †.
- **Filled sub-shells always have zero total spin and zero total angular momentum.** This is because we have to fill *all possible* m_l, m_s and at the same time maintain fermionic total anti-symmetry.
- Still reminiscent of the situation in Hydrogen, the binding energy of the outer electron jumps up (becomes much less negative) whenever $n \rightarrow n+1$, this gives periodic recurrence of chemical properties, mainly determined by outermost (valence) electron and how easily it is lost.
- The confusing middle part of the periodic table (transition metals) exists due to $3d \leftrightarrow 4s$ swap in the energy ordering (see † above) (This happens again for higher energy states $4d \leftrightarrow 5s, 4f \leftrightarrow 5d$).
- Note that all chemical variety in the world around us is due to the Pauli exclusion principle. Without it, any atom with varying nuclear charge Z would be just in a configuration $(1s)^Z$, thus all atoms would behave chemically very similar.

2.4.4 Approximation methods for many-electron systems

Thomas-Fermi theory: Assume electrons are (i) degenerate Fermi gas, (ii) numerous, (iii) can be treated in WKB/semi-classical approximation \implies Obtain electron charge density $\rho(\mathbf{r})$ and from that $V(\mathbf{r})$ (screened potential). Not very accurate, but interesting conceptually and useful in e.g. ultra-cold gases (also Bosons, see *Chapter-V*). Precursor to:

Density-functional theory: (Based on theorem by Hohenberg and Kohn)

For an N -electron system with ground-state wave function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, the ground-state electron density is

$$\rho(\mathbf{r}) = \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_3 \cdots \int d^3\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2. \quad (2.114)$$

Then,

- (a) every observable is uniquely determined by $\rho(\mathbf{r})$.
- (b) there exists a functional $I[\rho]$ such that for a given potential $U(\mathbf{r})$ (felt by all e^-), ground state energy is minimum of

$$E_o[\rho] = I[\rho] + \int d^3\mathbf{r} U(\mathbf{r})\rho(\mathbf{r}), \text{ for } \int d^3\mathbf{r} \rho(\mathbf{r}) = N.$$

- Useless unless we know $I[\rho]$. By now many "good" choices for $I[\rho]$ are available.
- Very successful method for quantum-chemistry/ material science.

Hartree-Fock method and the self-consistent field:

Idea: (i) Calculate $u_{nlm}(\mathbf{r})$ as in (2.105) using trial $V(\mathbf{r})$.

(ii) Calculate electron charge density $\rho(\mathbf{r}) = -e \sum |u_{nlm}(\mathbf{r})|^2$, this gives screening $V'(\mathbf{r})$.

(iii) Re-calculate $u'_{nlm}(\mathbf{r})$ with new $V'(\mathbf{r})$, iterate until converged.

(iv) In practice, this is all embedded in a many-body variational method, so won't directly recognize ρ, V .

Now, a sketch of derivation:

Use natural splitting of Hamiltonian (2.99)

$$\hat{H}_1 = \sum_{i=1}^N \hat{h}_i, \quad \hat{h}_i = -\frac{\nabla_{\mathbf{r}_i}^2}{2} - \frac{Z}{r_i}, \quad \hat{H}_2 = \sum_{i<j=1}^N \frac{1}{r_{ij}}, \quad \hat{H} = \hat{H}_1 + \hat{H}_2$$

from variational principle (2.89), the true ground-state energy E_0 fulfills

$$E_0 \leq E[\phi] = \langle \phi | \hat{H} | \phi \rangle, \quad (2.115)$$

but now ϕ is a many-electron Slater-determinant as in (2.110). Let us re-write

$$\phi(q_1, \dots, q_N) = \sqrt{N!} \mathcal{A} \phi_H(q_1, \dots, q_N) \quad (2.116)$$

with Hartree function:

$$\phi_H(q_1, \dots, q_N) = u_\alpha(q_1) u_\beta(q_2) \dots u_\nu(q_N). \quad (2.117)$$

$u_\alpha(q_i)$ etc. are again spin-orbitals, with form yet to be determined. We also used the anti-symmetrisation operator

$$\mathcal{A} \dots = \frac{1}{N!} \sum_{\mathcal{P}} (-1)^P \mathcal{P}[\dots] \quad (2.118)$$

Here the sum runs over all possible permutations \mathcal{P} of the set of integers $1 \dots N$, P is the sign of the permutation, and $\mathcal{P}[\dots]$ tells us to permute coordinates that occur within the brackets according to \mathcal{P} , i.e. $u_\alpha(q_1) u_\beta(q_2) \rightarrow u_\alpha(q_{\mathcal{P}[1]}) u_\beta(q_{\mathcal{P}[2]})$.

We now have to evaluate $E[\phi] = \langle \phi | \hat{H}_1 | \phi \rangle + \langle \phi | \hat{H}_2 | \phi \rangle$ for a Slater-determinant. We will use $[\hat{H}_i, \mathcal{A}] = 0$ (both \hat{H}_k are symmetric under all particle label swaps) and $\mathcal{A}^2 = \mathcal{A}$ (\mathcal{A} is a projector, if the expression in \dots is already anti-symmetrised, anti-symmetrising it again does nothing).

Now:

$$\begin{aligned} \langle \phi | \hat{H}_1 | \phi \rangle &\stackrel{\text{Eq. (2.116)}}{=} N! \langle \phi_H | \mathcal{A} \hat{H}_1 \mathcal{A} | \phi_H \rangle \stackrel{[\hat{H}_i, \mathcal{A}] = 0}{=} N! \langle \phi_H | \hat{H}_1 \mathcal{A}^2 | \phi_H \rangle \\ &\stackrel{\substack{\mathcal{A} \text{ is} \\ \text{projector}}}{=} N! \langle \phi_H | \hat{H}_1 \mathcal{A} | \phi_H \rangle \stackrel{\text{Eq. (2.118)}}{=} \sum_{i=1}^N \sum_{\mathcal{P}} (-1)^P \langle \phi_H | \hat{h}_i \mathcal{P} | \phi_H \rangle \end{aligned}$$

Now we can check that:

$$\langle \phi_H | \hat{h}_i \mathcal{P} | \phi_H \rangle = \begin{cases} \langle \phi_H | \hat{h}_i | \phi_H \rangle & ; \text{if } \mathcal{P} = \text{identity} \\ 0 & ; \text{else} \end{cases} \quad (2.119)$$

To see this explicitly expand the many-body scalar product as in the next step.

$$\begin{aligned} \langle \phi | \hat{H}_1 | \phi \rangle &= \sum_{i=1}^N \langle \phi_H | \hat{h}_i | \phi_H \rangle \\ &\stackrel{\text{Eq. (2.117)}}{=} \sum_{i=1}^N \int dq_1 \int dq_2 \underbrace{\dots}_{\text{No } i} \int dq_N \left(u_\alpha^*(q_1) u_\alpha(q_1) \right) \left(u_\kappa^*(q_{i-1}) u_\kappa(q_{i-1}) \right) \left(u_\eta^*(q_{i+1}) u_\eta(q_{i+1}) \right) \\ &\quad \left(u_\nu^*(q_N) u_\nu(q_N) \right) \left[\int dq_i \left(u_\lambda^*(q_i) \hat{h}_i u_\lambda(q_i) \right) \right] \\ &\stackrel{\text{all orbitals orthonormal}}{=} \sum_{i=1}^N \langle u_{\lambda_i}(q_i) | \hat{h}_i | u_{\lambda_i}(q_i) \rangle \equiv \sum_{i=1}^N I_{\lambda_i}; \quad \text{using an index vector } \vec{\lambda} = [\alpha, \beta, \dots, \nu]. \end{aligned}$$

The I_{λ_i} can be thought of as non-interacting energy of electron number i being in the spin-orbital $u_{\lambda_i}(q_i)$.

Similarly:

$$\begin{aligned} \langle \phi | \hat{H}_2 | \phi \rangle &= \sum_{i < j} \sum_{\mathcal{P}} (-1)^P \underbrace{\left\langle \phi_H \left| \frac{1}{r_{ij}} \mathcal{P} \right| \phi_H \right\rangle}_{\text{whenever } \mathcal{P} \text{ "touches" any index } \neq i, j \text{ this is } = 0} \\ &\stackrel{\text{only allowed permutation}}{=} \sum_{i < j} \left\langle \phi_H \left| \frac{1}{r_{ij}} (1 - \mathcal{P}_{ij}) \right| \phi_H \right\rangle \\ &\stackrel{\text{as above}}{=} \sum_{\substack{\lambda, \mu \\ \text{(Pairs)}}} \underbrace{\left\langle u_\lambda(q_i) u_\mu(q_j) \left| \frac{1}{r_{ij}} \right| u_\lambda(q_i) u_\mu(q_j) \right\rangle}_{\equiv \mathcal{J}_{\lambda\mu}} - \underbrace{\left\langle u_\lambda(q_i) u_\mu(q_j) \left| \frac{1}{r_{ij}} \right| u_\mu(q_i) u_\lambda(q_j) \right\rangle}_{\equiv \mathcal{K}_{\lambda\mu}} \\ &\quad \text{direct term, compare Eq. (2.97)} \quad \text{exchange term, compare Eq. (2.98)} \end{aligned}$$

In the second line, the only allowed permutations that don't give zero in the scalar product, is the identity (giving the 1), and \mathcal{P}_{ij} which flips $i \leftrightarrow j$.

- All together, we have now obtained a much simpler looking energy functional

$$E[\phi] = \sum_{\lambda} I_{\lambda} + \frac{1}{2} \sum_{\lambda\mu} [\mathcal{J}_{\lambda\mu} - \mathcal{K}_{\lambda\mu}]. \quad (2.120)$$

That consists of single particle energies I_{λ} and interaction energies J and K . The 1/2 just avoids double counting of pairs.

- Now, in a more complex variational principle than used for Helium, we vary all the $u_\lambda(q_i)$ themselves:

$$\delta E - \sum_{\lambda} \underbrace{E_{\lambda}}_{\text{Lagrange-multiplier}} \delta \langle u_{\lambda} | u_{\lambda} \rangle = 0. \quad (2.121)$$

(see math and book)

The Lagrange multipliers implement the constraint $\langle u_{\lambda} | u_{\lambda} \rangle = \delta_{\lambda\mu}$.

From variation $\delta u_{\lambda}(q_i)$ we obtain (see books)

Hartree-Fock equations:

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} \right] u_{\lambda}(q_i) + \left[\sum_{\mu} \int dq_j u_{\mu}^*(q_j) \frac{1}{r_{ij}} u_{\mu}(q_j) \right] u_{\lambda}(q_i) - \left[\sum_{\mu} \int dq_j u_{\mu}^*(q_j) \frac{1}{r_{ij}} u_{\lambda}(q_j) \right] u_{\mu}(q_i) = E_{\lambda} u_{\lambda}(q_i). \quad (2.122)$$

- Set of integer-differential, coupled equations for N spin orbitals $u_{\lambda}(q_i)$.
- Lagrange-multipliers E_{λ} take role of energy eigenvalues.
- We can define a direct potential

$$V^{(d)}(q_i) = \sum_{\mu} \int dq_j u_{\mu}^*(q_j) \frac{1}{r_{ij}} u_{\mu}(q_j)$$

and exchange potential (operator)

$$V^{(ex)}(q_i)[f] = \sum_{\mu} \left[\int dq_j u_{\mu}^*(q_j) \frac{1}{r_{ij}} f(q_j) \right] u_{\mu}(q_i)$$

such that

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} + \underbrace{V^{(d)} - V^{(ex)}}_{\equiv V(q_i)} \right] u_{\lambda}(q_i) = E_{\lambda} u_{\lambda}(q_i). \quad (2.123)$$

Comparison with Eq.(2.103), $V(q_i)$ takes the role of central field here.

- For atoms with filled subshells, can show that $V(q_i)$ is indeed spherically symmetric. Otherwise not, but derivations are small.
- Solve (2.122) by iteration: Start with some trial solution $u_{\lambda}^{(0)}(q_i)$ (e.g. the one for Hydrogen or guessed $V(q_i)$). Then find solution of

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} \right] u_{\lambda}^{(1)}(q_i) + \left[\sum_{\mu} \int dq_j u_{\mu}^{*(0)}(q_j) \frac{1}{r_{ij}} u_{\mu}^{(0)}(q_j) \right] u_{\lambda}^{(1)}(q_i) - \left[\sum_{\mu} \int dq_j u_{\mu}^{*(0)}(q_j) \frac{1}{r_{ij}} u_{\lambda}^{(0)}(q_j) \right] u_{\mu}^{(1)}(q_i) = E_{\lambda} u_{\lambda}^{(1)}(q_i). \quad (2.124)$$

etc. until $u_\lambda^{(n)}(q_i)$ is converged.

Example-(1) for section 2.4: Radial electron density in Neon

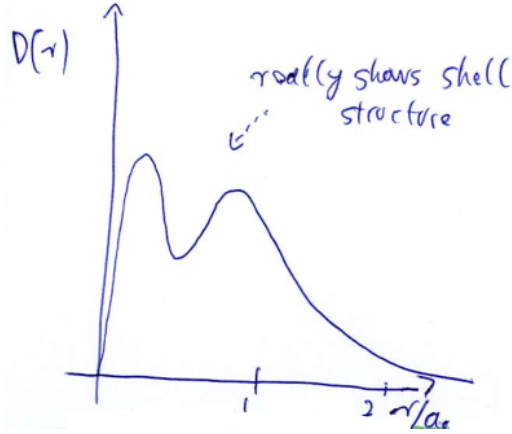
Define radial electron density

$$D(r) = r^2 \int \underbrace{d\Omega}_{\text{angles}} \rho(r) = \sum_{nl} \underbrace{g_{nl}}_{\substack{\# \text{ of equivalent electrons} \\ \text{in subshell } (nl)}} |\rho_{nl}(r)|^2. \quad (2.125)$$

Neon configuration $(1s)^2(2s)^2(2p)^6$, thus

$$D(r) = 2|P_{1s}(r)|^2 + 2|P_{2s}(r)|^2 + 6|P_{2p}(r)|^2.$$

which can be obtained via Eq. (2.122). The result is



2.4.5 Corrections to the central field. L-S/J-J coupling

There are two important correction terms to the central field picture discussed so far:

$$\hat{H}_1 = \sum_{i < j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z}{r_i} + V(\mathbf{r}_i) \right), \quad (2.126)$$

$$\hat{H}_2 = \sum_{i=1}^N \zeta_i(r) \hat{L}_i \cdot \hat{S}_i. \quad (2.127)$$

First is non-central field part of Hamiltonian, which we had listed as \hat{H}' in Eq. (2.102). Second spin-orbit coupling for each electron (c.f. Eq. (2.5)), the most important of relativistic corrections neglected in Eq. (2.99).

Which one is more important depends on Z .

L-S coupling (or Russell-Sanders coupling): : Warning: *L-S coupling means sth. very different from the words “spin-orbit coupling”!!*

L-S coupling is used for small or intermediate Z , in this case

$$|\hat{H}_1| \gg |\hat{H}_2| \text{ (nontrivial to link this to “small } Z\text{”).}$$

- First consider only \hat{H}_1 . \hat{H} commutes with \mathbf{J}_{tot} , \mathbf{L}_{tot} , \mathbf{S}_{tot} , see section 2.4.2.
- Determining which quantum numbers J , L , S are possible for a given state is nontrivial due to Pauli-exclusion principle⁰. Energy level with given fixed values of L , S is called a term.

Hund’s rules: For ground states:

- the term with the largest possible S for a given configuration has the lowest energy; energy then goes up as S goes down.
- for a given S , the term with maximum L has the lowest energy.

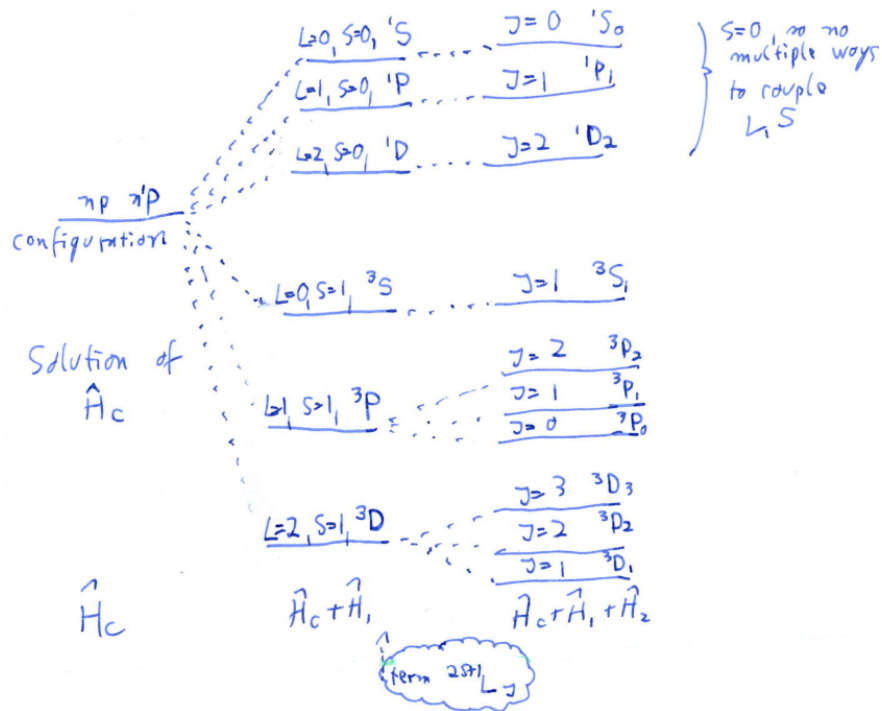
- So far we considered \hat{H}_1 only. Now we can add \hat{H}_2 as perturbation \rightarrow Fine-structure.
- Now each term with fixed L , S splits into separate J -components, which form a multiplett.
- Landé interval rule:

$$E(J) - E(J - 1) = \bar{A} \times J, \text{ within one multiplett,} \quad (2.128)$$

where \bar{A} is a constant. One finds $\bar{A} > 0$ for less than half filled shells, so that the ground-state has the lowest allowed J . However, $\bar{A} < 0$ for more than half filled shells, so that the ground-state then has the hightest allowed J .

⁰e.g. see section 4, helium ground-state can be only $L = 0$, not $L = 1$

Example-(2) for section 2.5: L-S coupling and fine-structure for two electrons



J-J coupling: This takes place for large Z ($Z \approx 80$), then we have $|\hat{H}_2| \gg |\hat{H}_1|$.

- **First:** $\hat{H}_c + \hat{H}_2 = \sum_{i=1}^N \hat{h}_i \rightarrow$ for each electron separately couple spin and angular momentum to j_k , giving orbitals u_{nljm_j} (based on $\hat{J}_i = \hat{L}_i + \hat{S}_i$).
- **Second:** We only then consider $\hat{H}_c + \hat{H}_2 + \hat{H}_1$ and have to label our many-electron state with $\hat{J} = \sum_{i=1}^N \hat{J}_i$, only labelled by J .

Example-(3) for section 2.5: J - J coupling

