

Can start in ψ , that was short

5

2.4. Many-electron atoms

- Already cannot solve $2e^-$ exactly. Variational approach also becomes too hard for large N_e . Central field approx. will be useful.

Many-electron (N) Schrödinger equation

$$\hat{H} \Psi(q_1, q_2, q_3, \dots, q_N) = E \Psi(q_1, q_2, \dots, q_N) \quad (2.36)$$

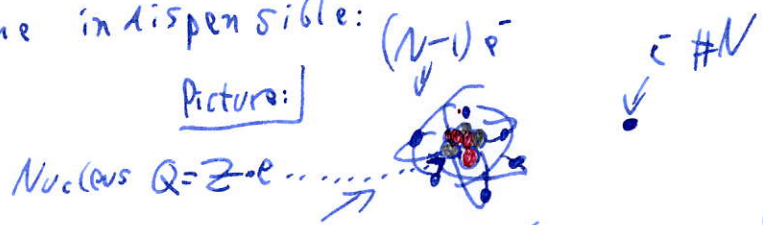
$q_n = \{ \sigma_n, \vec{r}_n \}$ (spin and position variables)

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

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

2.4.1. Central field approximation

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



Most important effect of other $(N-1)e^-$ is screening of nucleus, which leaves potential for N 'th electron radially symmetric

Similar to our He treatment we write for this ^{radial} potential felt by each electron

$$V(\vec{r}_i) = -\frac{Z}{|\vec{r}_i|} + S(r_i) \quad (\text{now screening is } r \text{ dependent}) \quad (2.37)$$

We also re-write Eq. (2.36) ignoring spin for now

$$\hat{H}_c = \sum_{i=1}^N \left(-\frac{\nabla_{\vec{r}_i}^2}{2} + V(\vec{r}_i) \right) = \sum_{i=1}^N \hat{h}_i \quad (2.37)$$

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

such that $\hat{H} = \hat{H}_c + \hat{H}'$ (just rewriting)

- \hat{H}_c is central field Hamiltonian
- expect ~~relationships~~ eigenfunctions of \hat{H}_c to be better than of $\hat{H}_0 = \sum_{i=1}^N \left(-\frac{\nabla_{\vec{r}_i}^2}{2} - \frac{Z}{r_i} \right)$
- challenge is to find suitable $S(\vec{r}_i)/V(\vec{r}_i)$

We can solve central field Schrödinger equation

$$\hat{H}_c \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E_c \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Using $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = u_{n_1, l_1, m_1}(\vec{r}_1) u_{n_2, l_2, m_2}(\vec{r}_2) \dots u_{n_N, l_N, m_N}(\vec{r}_N)$ $\{n_i, l_i, m_i\}$ $a_i \equiv$

where $\left[-\frac{1}{2} \nabla_{\vec{r}_i}^2 + V(\vec{r}_i) \right] u_{a_i}(\vec{r}_i) = E_i u_{a_i}(\vec{r}_i) \quad E_c = \sum E_i \quad (2.38)$

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

- As for hydrogen states we write $u_{n, l, m}(\vec{r}) = R_{n, l}(r) Y_{l, m}(\theta, \varphi)$ with $Y_{l, m}$ exact same as for H (spherical harmonics), but $R_{n, l}(r)$ determined from radial equation:

$$-\frac{1}{2} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R_{n, l}(r) + V(r) R_{n, l}(r) = E_{n, l} R_{n, l}(r) \quad (2.39)$$

\uparrow for Hydrogen due to screening

- Now: (2.39) $\xrightarrow{\text{determines}} u_{a_i}(\vec{r}_i) \xrightarrow{\text{determine}} e^- \text{ charge distribution} \rightarrow \text{screening } V(r):$

\Rightarrow requires self-consistent solution, see section

- Can learn a lot from known limits:

$$V(r) \rightarrow -\frac{Z}{r} \quad (\text{for } r \rightarrow \infty) \quad \text{and} \quad V(r) \rightarrow -\frac{Z - (N-1)}{r} \quad (2.39b) \quad \left(\text{for } r \rightarrow 0 \right)$$

2.4.2. Spin and Pauli exclusion principle

- Product states $\Psi(\vec{r}_1, \dots, \vec{r}_N) = u_{a_1}(\vec{r}_1) \dots u_{a_N}(\vec{r}_N)$ do not in general satisfy anti-symmetry requirements (Eq. 1.37) for Fermions, and we have not yet included spin ($\vec{r}_N \rightarrow q_N$, see Eq. 2.36)

Introduce spin-orbitals

$$u_{n\ell m m_s}(q) = u_{n\ell m}(r) |X_{m m_s}\rangle, \quad \text{with } |X_{+\frac{1}{2}}\rangle = |\uparrow\rangle \\ |X_{-\frac{1}{2}}\rangle = |\downarrow\rangle \quad (2.40)$$

$$= R_{n\ell}(r) Y_{\ell m}(\theta, \varphi) |X_{m m_s}\rangle$$

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

$$\Psi_c(q_1, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \dots & u_\nu(q_1) \\ u_\alpha(q_2) & & & \\ \vdots & & & \\ u_\alpha(q_N) & \dots & & u_\nu(q_N) \end{vmatrix} \quad (2.41)$$

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 $\alpha = \beta \Rightarrow \det = 0$ (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 (2.41) is called electron-configuration

- Note that $[\hat{H}_c, \hat{L}] = 0$, $[\hat{H}_c, \hat{S}] = 0$ for $(\hat{H}_c$ see Eq. (2.37))

total angular momentum (of all e^-) $\hat{L} = \sum_{i=1}^N \hat{L}_i$ (2.42)

total spin $\hat{S} = \sum_{i=1}^N \hat{S}_i$

Can write all many electron eigenstates also as eigenstates of \hat{L}, \hat{S} (not nec. the case for (2.41))

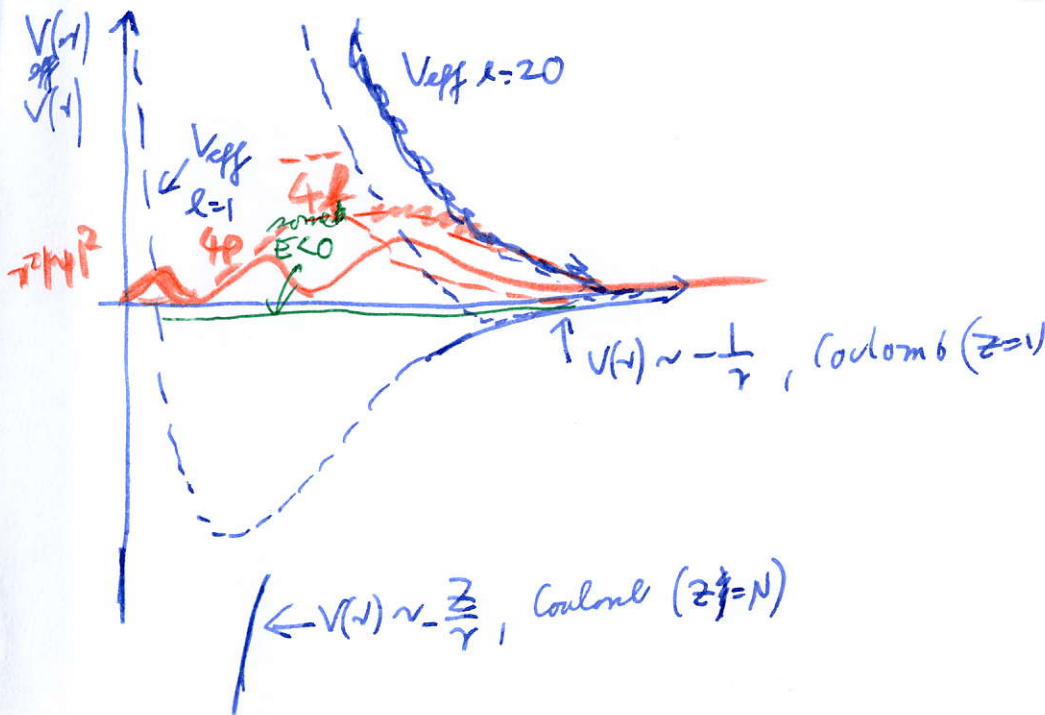
2.4.2. Groundstate energetic ordering and periodic table

- So far we have not really solved the many-electron-atom problem, since we did not yet calculate $S(r)$. But most ~~of~~ essential properties of all atoms (periodic table) can be understood already now, based on some $V(r)$ with properties (2.39b)

Angular Momentum versus screening: $[N=Z]$ Atoms

Revisit Eq. (2.39):
$$-\frac{1}{2} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R_{nl}(r) + V(r) R_{nl}(r) = E_{nl} R_{nl}(r)$$

$$V_{\text{eff}} = V(r) + \frac{l(l+1)}{2r^2}$$



- Centrifugal potential $\frac{l(l+1)}{2r^2}$ pushes wavelet further out, the higher l
- All higher l -states thus ~~feel~~ feel the unscreened $-\frac{Z}{r}$ potential less strongly and have higher energy

- Energy ~~expression~~ E_{nl} in Eq. (2.38) depends on all n, l (and not m_l, m_s while we ignore fine & hyperfine structure)
 \rightarrow electrons with same n, l are said to belong to the same sub-shell, and are also called equivalent electrons

- For values (n, l) , there are $2(2l+1)$ equivalent electrons (size of shell)

- To build periodic table, we fill shells from low energies

Table 8.3 book / www.ptable.com Projector

- \downarrow 4p states fill before 3d (3d has so much centrifugal pot.)
- Filled shells always have 1S_0 Term $(2s+2L, 0)$ (see section X?)

→ Reminiscent of Hydrogen energy jumps up when $n \rightarrow n+1$
 ↳ gives periodic recurrence of chemical properties, mainly given by outermost (valence) electron and how easy it is lost.

→ Confusing middle bit of periodic table (Transition metals) is all due to $3d \leftrightarrow 4s$ swap
 (later $4d \leftrightarrow 5s$, $4f \leftrightarrow 5d \dots$)

→ Note that all variety around us is due to Pauli exclusion principle, without which atom Z would be $(10)^Z$, and all atoms would behave chemically the same.

2.4.3. Approximation Methods for many-electron systems

Thomas-Fermi theory | Assume electrons are ~~interacting~~ ⁽ⁱ⁾ degenerate Fermi gas, (ii) numerous μ can be treated in WKB/semi-classical approximation. \Rightarrow obtain electron charge density $\rho(\vec{r})$ and from that $V(\vec{r})$ (screened potential). Not very accurate, but interesting conceptually & useful in e.g. ultra-cold ~~condensates~~ gases (also bosons, see chapter V)

Precursor to:

Density-functional theory:

Based on theorem by Hohenberg and Kohn

~~Kohn~~ For an N -electron system $\Psi(r_1, r_2, \dots, r_N)$, the _{w. ground state} ground-state electron density is

$$\rho(\vec{r}) = \int dr_2 dr_3 \dots dr_N |\Psi(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2 \quad (2.43)$$

Then (a) every observable is uniquely determined by $\rho(\vec{r})$

(b) There exists functional $I[\rho]$ such that for a given potential $U(\vec{r})$ [felt by all e^-], ground state energy is minimum of

$$E_0[\rho] = I[\rho] + \int U(\vec{r}) \rho(\vec{r}) d^3\vec{r}, \quad \text{for } \int \rho(\vec{r}) d^3\vec{r} = N$$

• Unless unless we know $I[\rho]$. By how many "good" $I[\rho]$ available

• Very successful method for quantum-chemistry / material science.

Hartree-Fock Method and the self-consistent field

- idea: (i) Calculate $U_{\text{em}}(\vec{r})$ as in (2.38) using trial $V(r)$
 (ii) Calculate electron charge density $\rho(\vec{r}) = -e \sum |U_{\text{em}}(\vec{r})|^2$,
 this gives screening $V'(r)$
 (iii) re-calculate $U_{\text{em}}(\vec{r})$ with new $V'(r)$, iterate until converged
 (iv) In practice this is all embedded in a many-body variational method, so won't directly recognize S, V_0 . Now sketch of derivation.

Use ^{natural} splitting of Hamiltonian (2.36)

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

From variational principle (2.3.2), groundstate energy

$$E_0 \leq E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle, \text{ but now } \Phi \text{ is a } \quad (2.43)$$

many-electron Slater determinant as in (2.41), let us rewrite

$$\Phi(q_1, \dots, q_N) = \sqrt{N!} \mathcal{A} \Phi_H(q_1, \dots, q_N) \quad (2.44)$$

with Hartree function:

$$\Phi_H(q_1, \dots, q_N) = u_\alpha(q_1) u_\beta(q_2) \dots u_\gamma(q_N) \quad (2.45)$$

$u_\alpha(q_i)$ etc. are again spin-orbitals, with form yet to be determined.

$$\mathcal{A} = \frac{1}{N!} \sum_P (-1)^P P \quad \text{is an anti-symmetrisation operator}$$

↑
: permutation operator

act on $q_1, q_2 \rightarrow q_2, q_1$ etc

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} symmetric under all particle label swaps]

and $\mathcal{A}^2 = \mathcal{A}$

[\mathcal{A} is a projector, if n th. is already antisymmetrised, second action no longer does anything]

Now:

$$\langle \Phi | \hat{H}_1 | \Phi \rangle \stackrel{\text{Eq. (2.44)}}{=} N! \langle \Phi_H | \mathcal{A} \hat{H}_1 \mathcal{A} | \Phi_H \rangle \stackrel{[\hat{H}_1, \mathcal{A}] = 0}{=} N! \langle \Phi_H | \hat{H}_1 \mathcal{A}^2 | \Phi_H \rangle$$

$$\stackrel{\mathcal{A} \text{ is projector}}{=} N! \langle \Phi_H | \hat{H}_1 \mathcal{A} | \Phi_H \rangle \stackrel{\text{Eq. (2.46)}}{=} \sum_{i=1}^N \sum_P (-1)^P \langle \Phi_H | \hat{h}_i P | \Phi_H \rangle$$

Now see:

$$\langle \Phi_H | \hat{h}_i P | \Phi_H \rangle \begin{cases} \stackrel{P=1}{=} \langle \Phi_H | \hat{h}_i | \Phi_H \rangle \\ \stackrel{\text{exp.}}{=} 0 \end{cases}$$

expand scalar-product if unclear (see next step 2)

$$\langle \Phi | \hat{H}_1 | \Phi \rangle = \sum_{i=1}^N \langle \phi_H | \hat{h}_i | \phi_H \rangle \stackrel{2.35}{=} \sum_{i=1}^N \int d\tau_1 \int d\tau_2 \dots \int d\tau_N (u_\alpha^*(q_i) u_\alpha(q_i)) (u_\beta^*(q_{i-1}) u_\beta(q_{i-1})) \dots (u_\nu^*(q_N) u_\nu(q_N))$$

$$\stackrel{\text{No } \lambda}{=} \int d\tau_1 \sum_{m_s} \int d\tau_2 \dots \int d\tau_N (u_\lambda^*(q_i) u_\lambda(q_i)) \hat{h}_i (u_\lambda(q_i))$$

all orbitals orthonormal
book uses \sum_λ

$$\sum_{i=1}^N \langle u_\lambda(q_i) | \hat{h}_i | u_\lambda(q_i) \rangle \stackrel{\approx}{=} \sum_{i=1}^N \int d\tau_i \text{ integration variable} \equiv \sum_{\lambda=1}^N I_\lambda$$

$\lambda_i = [\alpha \beta \dots \nu]$
(energies of individual Hamiltonian in orbitals)
 $u_\lambda(q_i)$

Similarly:

$$\langle \Phi | \hat{H}_2 | \Phi \rangle = \sum_{i < j} \sum_P (-1)^P \langle \phi_H | \frac{1}{r_{ij}} P | \phi_H \rangle$$

> 0 whenever P "touches" any index $\neq i, j$

only allowed permutation

$$\sum_{i < j} \langle \phi_H | \frac{1}{r_{ij}} (1 - P_{ij}) | \phi_H \rangle \stackrel{\text{above}}{=} \sum_{\lambda \mu \text{ (pairs)}} \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\lambda(q_i) u_\mu(q_j) \rangle - \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\mu(q_i) u_\lambda(q_j) \rangle$$

$\equiv K_{\lambda\mu}$ exchange-term
see Eq. (2.35)

All up: energy functional

$$E[\Phi] = \sum_\lambda I_\lambda + \frac{1}{2} \sum_{\lambda \mu} [J_{\lambda\mu} - K_{\lambda\mu}]$$

double count pairs

Now variational principle (we vary the $u_\lambda(q_i)$)

$$\delta E - \sum_\lambda \epsilon_\lambda \delta \langle u_\lambda | u_\lambda \rangle = 0 \quad (2.47)$$

Lagrange-multiplier (see Math & Book) Constraints: $\langle u_\lambda | u_\nu \rangle = \delta_{\lambda\nu}$

Assignment or Handout?

From variation $\delta u_\lambda(q_i)$ (leaves "coefficient" of replacement $u_\lambda \rightarrow \delta u_\lambda$)

Hartree-Fock equations:

$$\left[-\frac{1}{2} \nabla_{r_i}^2 - \frac{Z}{r_i} \right] u_\lambda(q_i) + \left[\sum_\mu \int d\tau_j u_\mu^*(q_j) \frac{1}{r_{ij}} u_\mu(q_j) \right] u_\lambda(q_i) - \left[\sum_\mu \int d\tau_j u_\mu^*(q_j) \frac{1}{r_{ij}} u_\lambda(q_j) \right] u_\mu(q_i) = E_\lambda u_\lambda(q_i) \quad (2.48)$$

- Set of integro-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 $V^d(q_i) = \sum_j \int d^3q_j u_{\mu}^*(q_i) \frac{1}{r_{ij}} u_{\mu}(q_j)$
 and exchange potential (operator) $V^e(q_i) = \sum_{\mu}^{\uparrow} \int d^3q_j u_{\mu}^*(q_i) \frac{1}{r_{ij}} \hat{P}[\mu] u_{\mu}(q_j)$

such that
$$\left[-\frac{1}{2} \nabla_{r_i}^2 - \frac{Z}{r_i} + V^d(q_i) - V^e(q_i) \right] u_{\lambda}(q_i) = E_{\lambda} u_{\lambda}(q_i) \quad (2.49)$$

Comparison with Eq. (2.38) $\equiv V(q_i)$ 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 deviations are small.

• Solve (2.48) by iterations Start with $u_{\lambda}^{(0)}(q_i)$ (eg. Hydrogen or guessed $V(q_i)$)

↳ Find solution of
$$\left[-\frac{1}{2} \nabla_{r_i}^2 - \frac{Z}{r_i} \right] u_{\lambda}^{(1)}(q_i) + \left[\sum_{\mu} \int d^3q_j u_{\mu}^{*(0)}(q_j) \frac{1}{r_{ij}} u_{\mu}^{(0)}(q_j) \right] u_{\lambda}^{(1)}(q_i) - \left[\sum_{\mu} \int d^3q_j u_{\mu}^{*(0)}(q_j) \frac{1}{r_{ij}} u_{\mu}^{(0)}(q_j) \right] u_{\lambda}^{(0)}(q_i) = E_{\lambda} u_{\lambda}^{(1)}(q_i)$$

 etc. until $u_{\lambda}^{(n)}(q_i)$ is converged ↖ ded 0/1

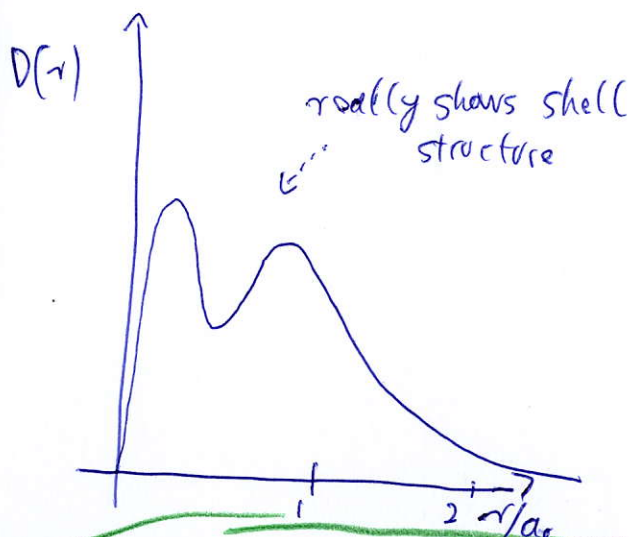
Example for section 2.4:

Radial electron density in Neon

Define $D(r) = r^2 \int_{\text{angles}} \rho(r) d\Omega = \sum_{nl} g_{nl} |p_{nl}(r)|^2$
 # of equivalent electrons in subshell (nl)

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

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



obtained via (2.48)

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

Two correction terms to central field picture discussed so far:

$$\hat{H}_1 = (\hat{H}' \text{ from (2.37)}) = \sum_{i < j}^N \frac{1}{r_{ij}} - \sum_i^N \left(\frac{Z}{r_i} + V(r_i) \right) \quad (2.50)$$

$$\hat{H}_2 = \sum_i \xi_i (-1) \hat{L}_i \cdot \hat{S}_i \quad (2.51)$$

First is "non-central" field part of Hamiltonian. Second spin-orbit coupling for each electron (c.f. Eq. (2.1)), the most important of relativistic corrections neglected in Eq. (2.36)

Need to consider ~~them~~ one or the other first dep. on Z (sameish as section 3.2.2 there it was dep. on $|B|$)

LS Coupling \leftarrow also Russell-Sanders coupling small / intermed Z

$|\hat{H}_1| \gg |\hat{H}_2|$ (nontrivial to link this to "small Z ")
 • First consider only \hat{H}_1 . \hat{H} commutes with $\vec{J}_{\text{tot}}, \vec{S}_{\text{tot}}, \vec{L}_{\text{tot}}$:

total angular momentum of electrons $\vec{J}_{\text{tot}} = \sum_{i=1}^N \vec{J}_i \quad (2.52)$
 total orbital $\vec{L}_{\text{tot}} = \sum_{i=1}^N \vec{L}_i$ [duplicate with (2.4)]
 total spin $\vec{S}_{\text{tot}} = \sum_{i=1}^N \vec{S}_i$

• Determining which J, L, S are possible for given state is nontrivial due to Pauli-exclusion principle. Energy level with given values of L, S is called term.

* e.g. see section 4, helium groundstate only $L=0$, no $L=1$

Hund's rules: For ground-states:

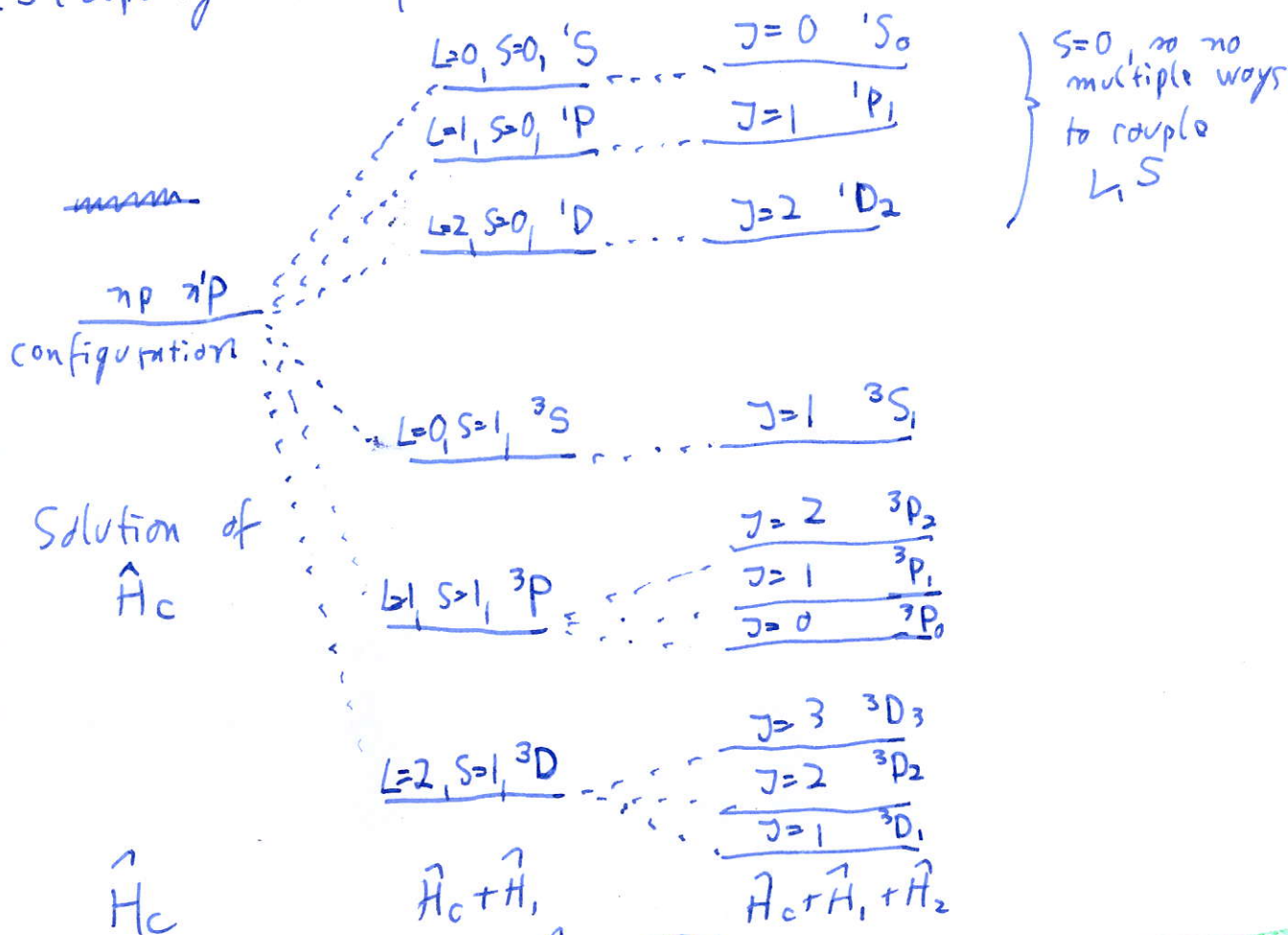
- term with largest possible S for a given configuration has the lowest energy; energy \uparrow as $S \downarrow$ (2.53)
- for given S , term with maximum L has lowest energy

• So for \hat{H}_1 only. Now add \hat{H}_2 as perturbation \rightarrow Fine structure
 • Now each term with fixed L, S splits into separate J components.

• Landé interval rule: $E(J) - E(J-1) = \text{const. } J$ (2.54)
 within one multiplett

Example 2 for section 2.5:

L-S coupling and fine-structure for two electrons



term $2S+1, L, J$

JJ coupling

$|\hat{H}_2| \gg |\hat{H}_1|$ large Z $Z \sim 80$

First: $\hat{H}_c + \hat{H}_2 = \sum_{i=1}^N \hat{h}_i \Rightarrow$ for each electron couple first $\hat{J}_i = \hat{L}_i + \hat{S}_i$
 \hookrightarrow orbitals l, m, m_s

Second: $\hat{H}_c + \hat{H}_2 + \hat{H}_1 \rightarrow \hat{J} = \sum \hat{J}_i$ coupling, only labelled by J

Example 3 for section 2.5:

