

# Quantum Mechanics II

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About the lecture:

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5 exercise groups: Mon/Tue: Sheets on web Thu: hints; Thu: hand-in; Thu: produce master solutions oral exam (heavily based on exercises)

Th: 22/2: other lecturer

If you find any mistakes / errors / problems with these notes, please write an e-mail to `pvecse@physik.uzh.ch`

## 1 Time-independent perturbation theory

### 1.1 Solving a Quantum Mechanical System

We have a standard QM system: given  $H$ ,  $|\psi(t_0)\rangle$ , we want to find  $|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle$ , we then get the time-evolution operator for  $H$  time independent

$$U(t, t_0) = \exp\left(-\frac{i}{\hbar} H \cdot (t - t_0)\right)$$

We have  $H = H^\dagger$ ,  $UU^\dagger = \mathbb{I}$ .  $H$  is self-adjoint,  $U$  is unitary.

“solution”: find all eigenvalues and eigenvectors  $|n\rangle$  of  $H$ , such that  $H|n\rangle = E_n|n\rangle$ . We have furthermore

$$H = \sum_n E_n |n\rangle \langle n| \quad \text{and} \quad U(t, t_0) = \sum_n e^{-\frac{i}{\hbar} E_n (t - t_0)} |n\rangle \langle n|$$

These are the spectral representations. We have the problem that only a small number of systems can be solved exactly (e.g. Coulomb potential, harmonic oscillator, infinite well,...). We therefore want to find approximate solutions. We can use perturbation theory and the variational method for that.

### 1.2 Non-degenerate case

We assume that  $H$  can be written as

$$H = \underbrace{H_0}_{\text{“free” Hamiltonian}} + \underbrace{\lambda V}_{\text{perturbation}}$$

The “free” Hamiltonian can be solved exactly. We know all the  $|n^{(0)}\rangle$ ,  $E_n^{(0)}$  with  $H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$  and  $\langle m^{(0)}|n^{(0)}\rangle = \delta_{mn}$

The perturbation is comparably “small”, for  $\lambda \rightarrow 0$  we get the free Hamiltonian, for  $\lambda \rightarrow 1$  we get the full Hamiltonian.

In section 1.2 we assume no degeneracy, i.e.  $E_n^{(0)} \neq E_m^{(0)} \quad \forall m \neq n$ .

We want  $|n\rangle$ ,  $E_n$ , such that  $H|n\rangle = E_n|n\rangle$

Let

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots + \mathcal{O}(\lambda^3)$$
$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots + \mathcal{O}(\lambda^3)$$

When doing perturbation theory, we always have to check in posteriori whether we get reasonable results. If the perturbation terms are bigger than the initial result, we might have to throw them away! Always take care to check well!

We then have to plug this expansion into the Schrödinger equation:

$$\begin{aligned}
& (H_0 - E_n^{(0)}) |n^{(0)}\rangle + \lambda((H_0 - E_n^{(0)}) |n^{(1)}\rangle + (V - E_n^{(1)}) |n^{(0)}\rangle) \\
& + \lambda^2 \left( (H_0 - E_n^{(0)}) |n^{(2)}\rangle + (V - E_n^{(1)}) |n^{(1)}\rangle - E_n^{(2)} |n^{(0)}\rangle \right) \\
& + \lambda^3 \left( (H_0 - E_n^{(0)}) |n^{(3)}\rangle + (V - E_n^{(1)}) |n^{(2)}\rangle - E_n^{(2)} |n^{(1)}\rangle - E_n^{(3)} |n^{(0)}\rangle \right) \\
& + \mathcal{O}(\lambda^4) = 0
\end{aligned}$$

We now look at the case of non-degenerate perturbation theory:

Let's first calculate the terms of order  $\lambda$ :

$$\begin{aligned}
& \langle m^{(0)} | H_0 - E_n^{(0)} | n^{(1)} \rangle + \langle m^{(0)} | V - E_n^{(1)} | n^{(0)} \rangle = 0 \\
& = \langle m^{(0)} | (E_m^{(0)} - E_n^{(0)}) | n^{(1)} \rangle + \langle m^{(0)} | V | n^{(0)} \rangle - E_n^{(1)} \underbrace{\langle m^{(0)} | n^{(0)} \rangle}_{\delta_{mn}} = 0
\end{aligned}$$

We now have two cases:

- $m = n$ :

$$\begin{aligned}
& \implies E_n^{(1)} = \langle n^{(0)} | V | n^{(0)} \rangle = \langle V \rangle_{n^{(0)}} \quad \boxed{\text{Eq1.2}} \\
& |n^{(1)}\rangle = \underbrace{\sum_m |m^{(0)}\rangle \langle m^{(0)} | n^{(1)} \rangle}_I = \sum_{m \neq n} |m^{(0)}\rangle \langle m^{(0)} | n^{(1)} \rangle + \underbrace{|n^{(0)}\rangle \langle n^{(0)} | n^{(1)} \rangle}_{=0 \text{ see below}} \\
& = \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)} | V | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}
\end{aligned}$$

- $m \neq n$ :

$$\begin{aligned}
1 = \langle n | n \rangle & = \underbrace{\langle n^{(0)} | n^{(0)} \rangle}_1 + \lambda \underbrace{\left( \langle n^{(0)} | n^{(1)} \rangle + \langle n^{(1)} | n^{(0)} \rangle \right)}_{=0} \implies \langle n^{(0)} | n^{(1)} \rangle = 0 \\
|n^{(1)}\rangle & = \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)} | V | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad \boxed{\text{Eq1.3}}
\end{aligned}$$

- $E_n^{(0)} = E_m^{(0)}$ : degenerate case
- $E_n^{(0)} \sim E_m^{(0)}$ : quasi-degenerate case

Now to the terms of order  $\lambda^2$ :

We now multiply with  $\langle k^{(0)} |$ :

$$\begin{aligned}
\boxed{\text{Eq1.4}} \quad & (E_k^{(0)} - E_n^{(0)}) \langle k^{(0)} | n^{(2)} \rangle + \langle k^{(0)} | V | n^{(1)} \rangle - E_n^{(1)} \underbrace{\langle k^{(0)} | n^{(1)} \rangle}_{\rightarrow 0} = E_n^{(2)} \underbrace{\delta_{kn}}_{\rightarrow 1} \\
E_n^{(2)} & = \langle n^{(0)} | V | n^{(1)} \rangle = \sum_{m \neq n} \frac{\langle n^{(0)} | V | m^{(0)} \rangle \langle m^{(0)} | V | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \\
& = \sum_{m \neq n} \frac{|\langle n^{(0)} | V | m^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \equiv \sum_{m \neq n} \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}
\end{aligned}$$

for the ground state ( $n = 0$ ), the 2<sup>nd</sup> order correction will always be negative  $E_n^{(2)} < 0$

$$|n^{(2)}\rangle = \sum_{m \neq n} |k^{(0)}\rangle \langle k^{(0)} | n^{(2)} \rangle + |n^{(0)}\rangle \langle n^{(0)} | n^{(2)} \rangle$$

The normalization of the wave function is then:

$$\begin{aligned} \langle n^{(0)} | n^{(2)} \rangle &= -\frac{1}{2} \langle n^{(1)} | n^{(1)} \rangle = -\frac{1}{2} \sum_{k \neq n} \frac{|V_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2} \\ \langle k^{(0)} | n^{(2)} \rangle &= \left( \frac{\langle k^{(0)} | V | n^{(1)} \rangle}{E_n^{(0)} - E_k^{(0)}} - \frac{E_n^{(1)} \langle k^{(0)} | n^{(1)} \rangle}{E_n^{(0)} - E_k^{(0)}} \right) \\ |n^{(2)}\rangle &= \sum_{k \neq n} \sum_{m \neq n} |n^{(0)}\rangle \frac{V_{kn} V_{mn}}{(E_n^{(0)} - E_k^{(0)}) (E_n^{(0)} - E_m^{(0)})} \\ &\quad - \sum_{k \neq n} \left( |k^{(0)}\rangle \frac{V_{mn} V_{kn}}{(E_n^{(0)} - E_k^{(0)})^2} + \frac{1}{2} |n^{(0)}\rangle \frac{|V_{kn}|^2}{(E_n^{(0)} - E_k^{(0)})^2} \right) \end{aligned} \quad \boxed{\text{Eq1.5}}$$

Step j: Look at  $(O)(\lambda^j)$  of Eq1.1:

- get  $E_n^j$
- get  $|n^{(j)}\rangle$

### 1.3 Degenerate perturbation theory

In this case, the energy level  $E_n^{(0)}$  of  $H_0$  is  $\alpha$ -fold degenerate:

$$H_0 |n_i^{(0)}\rangle = E_n |n_i^{(0)}\rangle \quad i = 1, \dots, \alpha$$

where  $|n_i^{(0)}\rangle$  is an orthonormal basis of eigenvectors of  $H_0$  with eigenvalue  $E_n$  and  $\langle n_i^{(0)} | n_j^{(0)} \rangle \sim \delta_{ij}$ . any linear combination

$$|\chi_n^{(0)}\rangle = \sum_{i=1}^{\alpha} c_{n_k, i} |n_i^{(0)}\rangle$$

is an eigenstate of  $H_0$  with eigenvalue  $E_n^{(0)}$ .

Typically, the perturbation  $V$  lifts the degeneracy (partially or completely) since usually  $[H_0, V] \neq 0$ .

Take  $E_{n_k}$  and  $|n_k\rangle$  with  $H |n_k\rangle = E_{n_k} |n_k\rangle$ . For  $\lambda \rightarrow 0$ ,  $E_{n_k} \rightarrow E_n^{(0)}$  and  $|n_k\rangle \rightarrow |\chi_{n_k}^{(0)}\rangle = \sum_{i=1}^{\alpha} c_{n_k, i} |n_i^{(0)}\rangle$ .

We then ask ourselves, which linear combination is the “good” one? We therefore have to find the coefficients  $c_{n_k, i} \forall n_k, k = 1, \dots, \alpha$ .

$$|n_k\rangle = |\chi_{n_k}^{(0)}\rangle + \lambda |n_k^{(1)}\rangle + \lambda^2 |n_k^{(2)}\rangle + \mathcal{O}(\lambda^3)$$

$$E_{n_k} = E_n^{(0)} + \lambda E_{n_k}^{(1)} + \lambda^2 E_{n_k}^{(2)} + \mathcal{O}(\lambda^3)$$

•

$$(H_0 - E_n^{(1)}) |n_k^{(1)}\rangle + (V - E_{n_k}^{(1)}) |\chi_{n_k}^{(0)}\rangle = 0$$

- multiply with  $\langle m_j^{(0)} |$ :

$$0 = (E_m^{(0)} - E_n^{(0)}) \langle m_j^{(0)} | n_k^{(1)} \rangle + \sum_{i=1}^{\alpha} c_{n_k, i} (\langle m_j^{(0)} | V | n_i^{(0)} \rangle - E_{n_k}^i \langle m_j^{(0)} | n_i^{(0)} \rangle)$$

- $n = m$  then one needs to solve:

$$0 = \sum_{i=1}^{\alpha} c_{n_k, i} (\langle n_j^{(0)} | V | n_i^{(0)} \rangle - E_{n_k}^{(1)} \delta_{ij}) = \sum_{i=1}^{\alpha} c_{n_k, i} (V_{ji} - E_{n_k}^{(1)} \delta_{ij}) \sim A \vec{x} = 0$$

- only non-trivial solution when

$$\text{Det} \begin{pmatrix} V_{11} - E_{n_k}^{(1)} & V_{12} & \dots & V_{1\alpha} \\ V_{21} & & & \\ \vdots & & & \\ \vdots & & & \\ V_{\alpha 1} & & & V_{\alpha\alpha} - E_{n_k}^{(1)} \end{pmatrix} = 0$$

This is an equation of order  $\alpha$  in the energies  $E_{n_k}^{(1)}$ , so we will get  $\alpha$  solutions.

- if all the solutions are different: degeneracy completely lifted
- if some of the solutions are the same: we still have partial (complete) degeneracy.

Once all the  $E_{n_k}^{(1)}$  are known, we can find the  $c_{n_k, i}$  (using linear algebra).

if  $V_{ij} = 0$  if  $i \neq j$ :

solutions  $E_{n_i}^{(1)} = \langle n_i^{(0)} | V | n_i^{(0)} \rangle$  (as in non-degenerate case)

→ try to find  $\chi_{n_k}^{(0)}$  such that  $\langle \chi_{n_i}^{(0)} | V | \chi_{n_j}^{(0)} \rangle = 0$  for  $i \neq j$ .

if there is an operator  $A$  with  $[A, V] = 0$  and eigenvectors/eigenvalues

$$A |\psi_{n_k}\rangle = a_{n_k} |\psi_{n_k}\rangle \text{ with } a_{n_k} \neq a_{n_i} \text{ for } i \neq k$$

then  $|\chi_{n_k}^{(0)}\rangle = |\psi_{n_k}\rangle$  does the job.

Proof:

$$\langle \psi_{n_i} | [A, V] | \psi_{n_j} \rangle = 0 = \underbrace{(a_{n_i} - a_{n_j})}_{\neq 0} \underbrace{\langle \psi_{n_i} | V | \psi_{n_j} \rangle}_{\Rightarrow = 0}$$

## 1.4 The Variational Method

Given a time-independent Hamiltonian  $H$  with a set of eigenvalues  $E_n$  and eigenvectors  $|\psi_n\rangle$

$$H |\psi_n\rangle = E_n |\psi_n\rangle$$

the for any arbitrary  $|\psi\rangle$  in the Hilbert space,

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0$$

Proof of Ritz theorem

We expand  $|\psi\rangle$  in eigenstates of  $H$ :

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle$$

$$\begin{aligned}\langle \psi | \psi \rangle &= \sum_{m,n} c_n^* c_m \underbrace{\langle \psi_n | \psi_m \rangle}_{\delta_{mn}} = \sum_n c_n^* c_n = \sum_n |c_n|^2 \\ \langle \psi | H | \psi \rangle &= \sum_{m,n} c_n^* c_m \underbrace{\langle \psi_n | H | \psi_m \rangle}_{E_m \langle \psi_n | \psi_m \rangle = E_m \delta_{mn}} = \sum_n |c_n|^2 E_m \\ \implies \langle H \rangle &= \frac{\sum_n E_n |c_n|^2}{\sum_n |c_n|^2}\end{aligned}$$

- Since  $|c_n|^2 \geq 0$  and  $E_n \geq E_0 \implies$

$$\langle H \rangle \geq E_0 \frac{\sum_n |c_n|^2}{\sum_n |c_n|^2} = E_0$$

- $E_0$  is a lower bound on  $\langle H \rangle$
- approximate  $E_0$  by minimizing of  $\langle H \rangle$  with respect to any parameter  $|\psi\rangle$  might depend on.

## 2 Hydrogen Atom

### 2.1 Coulomb potential (QMI)

General 2-body-problem  $(m_1, \vec{r}_1), (m_2, \vec{r}_2) \rightarrow V(\vec{r}_1 - \vec{r}_2)$  (with no external interactions). We then write down the Hamiltonian:

$$H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\vec{r}_1 - \vec{r}_2)$$

$\nabla_1$  acts on  $\vec{r}_1$ ,  $\nabla_2$  acts on  $\vec{r}_2$ . We have a wave function  $\Psi(\vec{r}_1, \vec{r}_2)$  ( $\otimes$  spin d.o.f. as in classical mechanics, separate centre-of-mass variables. We introduce

$$\vec{r}_1, \vec{r}_2 \rightarrow \vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \text{ and } \vec{r} = \vec{r}_1 - \vec{r}_2$$

We then rewrite the Hamiltonian:

$$H = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \text{ with } M = m_1 + m_2 \text{ and } m = \frac{m_1 m_2}{m_1 + m_2}$$

We then want to find the eigenstates:

$$H |\Psi(\vec{R}, \vec{r})\rangle = E_{\text{tot}} |\Psi(\vec{R}, \vec{r})\rangle$$

we separate the variables:  $\Psi(\vec{R}, \vec{r}) = \phi(\vec{R})\psi(\vec{r})$  in order to get two separate differential equations:

$$-\frac{\hbar^2}{2M} \nabla_R^2 \phi(\vec{R}) = E_R \phi(\vec{R}) \quad \text{free particle ("boring")}$$

We are looking for bound states.

$$-\frac{\hbar^2}{2m} \nabla_r^2 \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E_r \psi(\vec{r}) \quad \text{particle in potential } V(\vec{r})$$

Only the relative motion is interesting. The nice thing about the Coulomb potential is that  $V(\vec{r}) = V(r)$ , the potential only depends on the absolute value of  $\vec{r}$ . In the hydrogen atom we have:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right) \psi(\vec{r}) = E \psi(\vec{r})$$

We have  $V(r) = -\frac{Ze^2}{r}$  in Gauss units. From QMI we know we can write

$$\psi(\vec{r}) = R_{El}(r)Y_l^m(\theta, \varphi) = \frac{u_{El}(r)}{r}Y_l^m(\theta, \varphi)$$

We then get by applying the differential equation:

$$u_{El}'' - \left( \frac{l(l+1)}{r^2} + \frac{2m(V(r) - E)}{\hbar^2} \right) u_{El} = 0$$

We then get the possible eigenvalues for bound states:

$$E_n = - \left( \frac{Ze^2}{\hbar^2} \right)^2 \frac{m}{2n^2} = - \frac{(Ze)^2}{2n^2} \frac{1}{a} = - \frac{(Z\alpha)^2}{2n^2} mc^2 \text{ with } \alpha = \frac{e^2}{\hbar c} \sim \frac{1}{137} \text{ and } a = \frac{\hbar^2}{me^2}$$

We know that this system is very degenerate. The degeneracy for one particular value of  $n$  is:

$$l : 0, 1, \dots, n-1$$

$$m_l : -l, -l+1, \dots, 0, \dots, l-1, l$$

For a fixed  $n$  we get:

$$\underbrace{2}_{\text{spin}} \sum_{l=0}^{n-1} (2l+1) = 2n^2$$

The wave functions are:

$$\Psi_{nlm_l} = |n, l, m\rangle \sim (\text{Laguerre polynomial}) \cdot Y_l^{m_l}$$

Now we include further effects:

- relativistic effects
- spin of electron
- spin of proton
- (QFT effects)

These effects will partially lift the  $n^2$  degeneracy.

Warning: in this section we will cheat in the derivation of the Hamiltonian → do properly at end of the course (hopefully)

## 2.2 Relativistic corrections

We use the non-relativistic Schrödinger equation.

Is this justified? Look at expectation value of velocity:

$$\langle v \rangle = \langle n, l, m | \frac{p}{m} | n, l, m \rangle = \dots = \frac{Z\alpha}{n^2}$$

This shows that the non-relativistic approach is ok.  $(Z\alpha) \ll 1 \implies$  non-relativistic system.

The kinetic energy is

$$T = \frac{p^2}{2m} \rightarrow \sqrt{p^2c^2 + m^2c^4} - mc^2 = \frac{p^2}{2m} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{small} \rightarrow \text{use perturbation theory}} + \underbrace{\dots}_{\text{neglected}} \text{ relativistic energy}$$



We are interested in the shift of the energy levels due to the perturbation. This can be calculated as follows:

$$\begin{aligned}\Delta E_{\text{rel}} &= -\langle n, l, m_l | \frac{p^4}{8m^3c^2} | n, l, m_l \rangle = -\frac{1}{2mc^2} \langle n, l, m_l | \underbrace{\left( \frac{p^2}{2m} \right)^2}_{(H_0 + \frac{Ze^2}{r})^2} | n, l, m_l \rangle \\ &= \frac{1}{2mc^2} \left\langle n, l, m_l \left| \left( H_0 + \frac{Ze^2}{r} \right) \left( H_0 + \frac{Ze^2}{r} \right) \right| n, l, m_l \right\rangle \\ &= -\frac{1}{2mc^2} \left( (E_n^{(0)})^2 + 2E_n^{(0)} Ze^2 \left\langle \frac{1}{r} \right\rangle_{nlm} + (Ze^2)^2 \left\langle \frac{1}{r^2} \right\rangle_{nlm} \right)\end{aligned}$$

or all  $\langle \frac{1}{r^n} \rangle$  in the exercises  
Results for this are:

$$\begin{aligned}\left\langle \frac{1}{r} \right\rangle_{nlm_l} &= \frac{Z}{an^2} \\ \left\langle \frac{1}{r^2} \right\rangle_{nlm_l} &= \frac{Z^2}{a^2n^3(l + \frac{1}{2})} \\ \left\langle \frac{1}{r^3} \right\rangle_{nlm_l} &= \frac{Z^3}{a^3n^2l(l + \frac{1}{2})(l + 1)} \text{ with } l \neq 0\end{aligned}$$

This can then be used to calculate  $\Delta E_{\text{rel}}$ :

$$\Delta E_{\text{rel}} = -E_n^{(0)} \underbrace{\frac{Z^2\alpha^2}{\text{small} \rightarrow :)}_{\frac{1}{n^2}} \left( \frac{3}{4} - \underbrace{\frac{n}{l + \frac{1}{2}}}_{\text{dependence on } l} \right)$$

This whole thing we are calculating here is part of the fine structure. So they are proportional to the fine structure constant.

### 2.3 Spin-Orbit term

Now: naive and rough “derivation” of the perturbation term in the Hamiltonian. Argumentation: in the rest frame of the electron, the moving proton induces a magnetic field. This field acts on the spin of the electron.

- $e^-$  with spin  $\rightarrow$  magnetic moment :  $\vec{\mu} = \frac{e}{2m}g\vec{s}$  with  $g \approx 2$  (from Dirac equation, or better, from QED)
- The magnetic field is roughly

$$\vec{B} \sim -\frac{1}{c^2} \vec{v} \wedge \underbrace{\vec{E}}_{e \frac{\vec{r}}{r^3}} \sim -\frac{1}{mc^2 r^3} \vec{p} \wedge \vec{r} \sim -\frac{\vec{L}}{mc^2 r^3}$$

The correct result for the Hamiltonian is then

$$H_{SO} = \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \vec{L} \cdot \vec{S} \quad \left( \sim -\vec{\mu} \cdot \vec{B} \right)$$

To describe the spin of the electron

$$|n, l, m_l, (s), m_s\rangle = \Psi_{nlm_l m_s} = \underbrace{\Psi_{nlm_l}(r, \theta, \varphi)}_{L^2[\mathbb{R}^2]} \otimes \underbrace{\chi_{s=\frac{1}{2}, m_s}}_{\mathbb{C}^2}$$

1<sup>st</sup> order perturbation theory:

$$\Delta E_{SO} = \langle n, l, m_l, m_s | H_{SO} | n, l', m_l', m_s \rangle$$

$$\Delta E_{SO} = 0 \text{ for } l' \neq l, \text{ because } [\vec{L}^2, H_{SO}] \sim [\vec{L}^2, \vec{L} \cdot \vec{S}] = 0$$

for fixed  $n, l$ :  $2 \cdot (2l + 1)$ -dimensional subspace of Hilbert Space  $n, l, m_l$  and  $m_s$  are not ideal quantum numbers, we change quantum numbers because of this. We take instead  $j, m_j$

$$\vec{J} = \vec{L} + \vec{S}$$

$$j : l \pm \frac{1}{2}, \quad m_j : -j, -j + 1, \dots, j, \quad (j = \frac{1}{2} \text{ for } l = 0)$$

from

$$\vec{J}^2 = (\vec{L} + \vec{S})^2 = \vec{L}^2 + 2\vec{L} \cdot \vec{S} + \vec{S}^2$$

$$H_{SO} \supset \vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$$

“good” eigenstates in which  $\vec{L} \cdot \vec{S}$  is diagonal:

$$|n, l, (s), j, m_j\rangle = \sum \underbrace{\langle l, s, m_l, m_s | j, m_j \rangle}_{\text{Clebsch-Gordan coefficients}} \cdot |n, l, m_l, (s), m_s\rangle$$

We can then again use perturbation theory: evaluate:

$$\Delta E_{SO} = \langle n, l, j, m_j | \frac{\vec{L} \cdot \vec{S}}{r^3} | n, l, j, m_j \rangle \frac{Ze^2}{2m^3c^2} = \left\langle \frac{1}{r^3} \right\rangle \frac{Ze^2}{2m^3c^2} \frac{1}{2} \left( j(j+1) - l(l+1) - \frac{3}{4} \right)$$

$$H_{rel} : \quad : \langle n, l, m_l, \dots | H_{Rel} | n, l', m_l', \dots \rangle$$

In principle it is degenerate perturbation theory but already diagonal.

$$H_{SO} : \quad : \langle n, l, m_l, \dots | H_{SO} | n, l, m_l', \dots \rangle$$

use “good” basis  $\rightarrow$  diagonalize

$$\begin{aligned} \rightarrow \Delta E_{SO} &= \frac{Ze^2}{2mc^2} \left\langle n, l, j, m_j \left| \frac{1}{r^3} \frac{1}{2} \left( \underbrace{\vec{J}^2 - \vec{L}^2 - \vec{S}^2}_{\vec{J}=\vec{L}+\vec{S}=\vec{L} \otimes \mathbb{1} + \mathbb{1} \otimes \vec{S}} \right) \right| n, l, j, m_j \right\rangle \\ &= \frac{Ze^2 \hbar^2}{4mc^2} \left\langle \frac{1}{r^3} \right\rangle_{nl} \left( j(j+1) - l(l+1) - \frac{3}{4} \right) \end{aligned}$$

This then gives us the following result:

$$\Delta E_{SO} = \begin{cases} 0, & l = 0 \\ E_n^{(0)} \frac{(Z\alpha)^2}{2n(l+\frac{1}{2})} \cdot \frac{1}{l+1}, & j = l + \frac{1}{2} \\ E_n^{(0)} \frac{(Z\alpha)^2}{2n(l+\frac{1}{2})} \cdot \frac{-1}{l}, & j = l - \frac{1}{2} \end{cases}$$

## 2.4 Darwin term

The position of the electron fluctuates in the order of magnitude of the Compton wavelength  $\lambda_C \sim \frac{\hbar}{mc}$ . The electron feels the average potential  $\langle V(r + \delta r) \rangle = \langle V(r) \rangle + \frac{1}{2} \langle (\delta r)(\nabla \delta r) \nabla V(r) \rangle = \langle V(r) \rangle + \frac{1}{2} \langle (\delta \vec{r})^2 \Delta V(r) \rangle \sim \langle V(r) \rangle + \frac{1}{2} \left\langle \frac{\hbar^2}{m^2 c^2} (4\pi \delta(r)) Z e^2 \right\rangle$

$$\implies \boxed{H_D = \frac{\pi \hbar^2 Z e^2}{2m^2 c^2} \delta(r)}$$

This term picks the wave function at the origin. It is therefore only relevant for  $l = 0$ , otherwise it is zero, because for  $l \geq 1$ , the probability amplitude at the origin is zero.

$$\Delta E_D = \langle n, l, j, m_j | H_D | n, l, j, m_j \rangle = \frac{\pi \hbar^2 Z e^2}{2m^2 c^2} |\Psi_{nl}(0)|^2 = -E_n^{(0)} \frac{(Z\alpha)^2}{n} \delta_{l0}$$

## 2.5 Fine structure of hydrogen

We now want to combine all the terms we have calculated:

$$\begin{aligned} \Delta E^{(1)} &= \Delta E_{rel} + \Delta E_{SO} + \Delta E_D \\ \rightarrow \Delta E_{n,j}^{(1)} &= -E_n^{(0)} \frac{(Z\alpha)^2}{n^2} \left( \frac{3}{4} - \frac{n}{j + \frac{1}{2}} \right) \end{aligned}$$

This formula is valid for  $l = 0, j = l \pm \frac{1}{2}, \forall l$ . So the degeneracy is partially lifted.

Spectrum: notation for states:  ${}_n L_J$  with  $n = 1, \dots, l = 0, 1, \dots, n-1, L = S, P, D, \dots, J$ : total angular momentum

Symbol (degeneracy)	l=0	l=1	l=2	number of states = $2 \times n^2$
n=1	${}_1 S_{1/2}$ (2)	×	×	$2 = 2 \times 1^2$
n=2	${}_2 S_{1/2}$ (2)	${}_2 P_{3/2}$ (4), ${}_2 P_{1/2}$ (2)	×	$8 = 2 \times 2^2$
n=3	${}_3 S_{1/2}$ (2)	${}_3 P_{3/2}$ (4), ${}_3 P_{1/2}$ (2)	${}_3 D_{5/2}$ (6), ${}_3 D_{3/2}$ (4)	$18 = 2 \times 3^2$

$({}_2 S_{1/2}) \leftrightarrow ({}_2 P_{1/2})$  is, if we look precisely at the experiment, still degenerate after taking in to account the fine structure. This is because of smaller effects that lift this degeneracy:

- hyperfine structure (spin-spin)
- QFT effects

Now we stop QM1 and start QM2.

## 3 Many electron atoms

We now consider an atom with  $N$  electrons.

$$H\Psi(\underbrace{1}_{\vec{r}_1, \vec{s}_1, \text{other quantum numbers}}, 2, \dots, N) = E\Psi(1, 2, \dots, N)$$

We can now easily write down the Hamiltonian:

$$H = \underbrace{\sum_{i=1}^N \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right)}_{\text{easy}} + \underbrace{\sum_{i>j} \frac{e^2}{|r_i - r_j|}}_{\text{killer}}$$

This is a complicated problem which cannot be solved exactly even for  $N = 2$ . We therefore have to use approximations.

### 3.1 Identical particles

Consider  $N$  identical particles  $H(1, 2, \dots, N)$ ,  $\Psi(1, 2, \dots, N)$  In Classical Mechanics you can always distinguish the  $N$  particles.

In Quantum Mechanics you cannot keep track of individual particles, because the wave function might overlap.

We now define the permutation operator  $P_{ij}$  that interchanges the two particles  $i$  and  $j$ .

$$P_{ij}\Psi(1, \dots, i, \dots, j, \dots, N) = \Psi(1, \dots, j, \dots, i, \dots, N) \quad P_{ij}^2 = \mathbb{I}$$

$P_{ij}$  has the eigenvalues  $\pm 1$ .

$H$  must be invariant under  $P_{ij}$ :  $[H, P_{ij}] = 0$ .

There are  $N!$  permutations of the arguments of  $\Psi(1, 2, \dots, N)$ . The permutations fall into two classes: even and odd. The signum of  $P$  is  $(-1)^{\text{number of interchanges needed}}$ .

$$\begin{cases} \text{sgn}(P) = +1 = (-1)^P, & P \text{ even (number of interchanges } P_{ij}) \\ \text{sgn}(P) = -1 = (-1)^P, & P \text{ odd (number of interchanges } P_{ij}) \end{cases}$$

We know certain things about  $P$ :

- we have  $[P, H] = 0$
- $P$  is unitary:  $\langle \chi | \Psi \rangle = \langle P\chi | P\Psi \rangle = \left\langle \chi \left| \underbrace{P^\dagger P}_{\mathbb{I}} \right| \Psi \right\rangle$
- for any observable  $A$ :  $[A, P] = 0$ :  $\langle P\chi | A | P\Psi \rangle = \langle \chi | P^\dagger A P | \Psi \rangle = \langle \chi | P^\dagger P A | \Psi \rangle = \langle \chi | A | \Psi \rangle$
- since  $[P_{ij}, P_{ik}] \neq 0$ : An eigenstate of  $A$  is not in general an eigenstate of all  $P_{ij}$ .

There are 2 special cases: the totally symmetric combination:  $|\Psi_S\rangle$ , with  $P|\Psi_S\rangle = |\Psi_S\rangle$  and the totally antisymmetric combination:  $|\Psi_A\rangle$ , with  $P_{ij}|\Psi_A\rangle = -|\Psi_A\rangle$  and  $P|\Psi_A\rangle = \text{sgn}(P)|\Psi_A\rangle$  e.g.  $N=3$ :

$$|\Psi_S\rangle = \frac{1}{\sqrt{3!}} (\Psi(1, 2, 3) + \Psi(1, 3, 2) + \Psi(2, 1, 3) + \Psi(2, 3, 1) + \Psi(3, 1, 2) + \Psi(3, 2, 1))$$

$$|\Psi_A\rangle = \frac{1}{\sqrt{3!}} (\Psi(1, 2, 3) + \Psi(2, 3, 1) + \Psi(3, 1, 2) - \Psi(3, 2, 1) - \Psi(2, 1, 3) - \Psi(1, 3, 2))$$

Spin-statistics theorem: particles with integer spin (bosons) are described by symmetric wave functions  $|\Psi_S\rangle$ , particles with half-integer spin (fermions) are described by antisymmetric wave functions  $|\Psi_A\rangle$ .

We now look at a Hamiltonian

$$H = \sum_{i=1}^N H_i \quad (\text{non-interacting identical particles})$$

We now write  $\Psi(1, 2, \dots, N) = \prod_{i=1}^N \Psi_i(i)$  with  $H_i \Psi_i = E_i \Psi_i$  and  $H\Psi(1, \dots, N) = (\sum E_i) \Psi(1, \dots, N)$  Then we have: Bosonic case:

$$\Psi_S(1, \dots, N) = \frac{1}{\sqrt{N!}} \sum_P \Psi_1(\vec{r}_{P(1)}, \vec{s}_{P(1)}) \dots \Psi_n(\vec{r}_{P(N)}, \vec{s}_{P(N)})$$

Fermionic case:

$$\Psi_A(1, \dots, N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \Psi_1(P(1)) \dots \Psi_N(P(N))$$

This can then be written as Slater determinant

$$\Psi_A(1, \dots, N) = \frac{1}{\sqrt{N!}} \text{Det} \begin{pmatrix} \Psi_1(1) & \dots & \Psi_1(N) \\ \vdots & & \vdots \\ \Psi_N(1) & \dots & \Psi_N(N) \end{pmatrix}$$

We then get the : Pauli exclusion principle: Two identical fermions cannot be in the same state.  
Application: Fermi gas with the Fermi energy and its other properties.

### 3.2 Thomas-Fermi approximation

The Thomas-Fermi approximation is a semi-classical approximation for large  $Z$ . Each electron feels the average spherically symmetrical potential  $\Phi(r)$ , created by the nucleus and the other electrons. The potential then changes as follows:

$$V(r) = -\frac{Ze^2}{r} \rightarrow -e\Phi(r)$$

We now look at the Poisson equation for this  $\Phi(r)$ :

$$\nabla^2 \Phi(r) = -4\pi \underbrace{\tilde{\rho}}_{r>0} = 4\pi e\rho \quad \text{with } \tilde{\rho}(r) = \underbrace{-e\rho(r)}_{\text{all } e^-} + Ze\delta(r)$$

$\Phi$  and  $\rho$  are related. Let  $n$  be the number of  $e^-$  states in a particular energy range.

$$n = \frac{2}{(2\pi\hbar)^2} \quad \text{if } E = \frac{p_F^2}{2m} - e\Phi < 0$$

$$n = 0 \quad \text{if } E > 0$$

The 2 comes from the spin of the electron.

We then write  $\rho$ :

$$\rho = \int_{|\rho| < \sqrt{2me\Phi}} nd^3p = \frac{2 \cdot 4\pi}{(2\pi\hbar)^3} \int_0^{\sqrt{2me\Phi}} p^2 dp = \frac{8\pi}{3(2\pi\hbar)^3} (2me\Phi)^{3/2}$$

We plug this into the Poisson equation, in order to get an equation for  $\Phi$ :

$$\nabla^2 \Phi(r) = \frac{1}{r} \frac{d^2}{dr^2} r\Phi(r) = \frac{32\pi^2 e}{3(2\pi\hbar)^3} (2me\Phi(r))^{3/2}$$

We have assumed that  $Z$  is large, so this approximation only works reasonable for the case of big atoms. Furthermore we have to carefully look at the boundary conditions of this differential equation:

$$\text{Nucleus: } \Phi(r) \rightarrow \frac{Ze}{r} \text{ for } r \rightarrow 0$$

$$\text{Normalization: } 4\pi \int \rho(r)r^2 dr = Z$$

The differential solution can be solved numerically. [Plot,  $\Phi(r)$  looks roughly like something  $r^{-\alpha}$ ]. This plot shows that using this approximation the electron density stretches until infinity (a failure of the model). For small  $r$  we get:

$$\Phi(r) \sim \frac{Ze}{r} - \underbrace{\text{cst.}}_{\sim 2} \cdot Z^{4/3} \frac{e}{a}$$

We can define a radius  $R(\eta)$ , which is the radius that contains all but the fraction  $\eta$  of the electrons:

$$(1 - \eta)Z = \int^{R(\eta)} 4\pi\rho(r)r^2 dr$$

If you ask for the radius within which all but one  $e^-$  are:

$$R\left(\frac{1}{Z}\right) \sim \text{const.} \cdot Z^{-1/3}a$$

### 3.3 The Hartree approximation

Assume  $\Psi(1, \dots, N) = \varphi_1(1) \cdot \varphi_2(2) \cdots \varphi_N(N)$  as a solution to  $H = \sum_i \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{|r_i - r_j|}$ .

Note: this contradicts Fermi statistics. The statistics is partially taken into account by forcing  $\varphi_i(i)$  to be distinct (orthogonal). Furthermore there is a normalization condition:  $\int d^3r_i |\varphi_i(i)|^2 = 1$

We now want to find a stationary state w.r.t. to variation in  $\varphi_i(i)$ .  $\rightarrow$  functional derivative

$$\langle H \rangle = \sum_i \int d^3\vec{r}_i \left( \varphi_i^*(\vec{r}_i) \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{|r_i|} \right) \varphi_i(\vec{r}_i) \right) + \sum_{i>j} \int d^3\vec{r}_i \int d^3\vec{r}_j \varphi_i^*(\vec{r}_i) \varphi_j^*(\vec{r}_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \varphi_i(\vec{r}_i) \varphi_j(\vec{r}_j)$$

We now want to minimize this under constraints  $0 = \int d^3\vec{r}_i |\varphi_i(\vec{r}_i)|^2 - 1$ . We do this with Lagrange multipliers. We call our Lagrange multipliers  $\varepsilon_i$ . We want to minimize

$$\langle H \rangle - \sum_j \varepsilon_j \left( |\varphi_j|^2 - 1 \right)$$

$$= \sum_i \int d^3\vec{r} \left( \varphi_i^*(\vec{r}_i) \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{|r_i|} - \varepsilon_i \right) \varphi_i(\vec{r}_i) + \varepsilon_i \right) + \sum_{i>j} \int d^3\vec{r}_i \int d^3\vec{r}_j \varphi_i^*(\vec{r}_i) \varphi_j^*(\vec{r}_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \varphi_i(\vec{r}_i) \varphi_j(\vec{r}_j)$$

This is an MMP problem. This whole thing is a functional, so we have to use the appropriate techniques to minimize it. This is done by using functional derivatives with respect to  $\frac{\delta}{\delta \varphi_i^*(\vec{r}_i)}$ . This will then give us an equation for the function  $\varphi_i(\vec{r}_i)$ .

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{|r_i|} + V_i(\vec{r}_i) \right) \varphi_i(\vec{r}_i) = \varepsilon_i \varphi_i(\vec{r}_i)$$

$$V_i(\vec{r}_i) = \sum_{j \neq i} \int d^3\vec{r}_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} |\varphi_j(\vec{r}_j)|^2$$

These equations are hard to solve, since  $V_i(\vec{r}_i)$ , the potential acting on the electron  $i$ , depends on all the other electrons.

These equations are usually solved iteratively.

We first assume  $\varphi_i^{(0)}, \dots, \varphi_N^{(0)} \rightarrow V^{(0)}$

$\varphi_i^{(1)}, \dots, \varphi_N^{(1)} \rightarrow V^{(1)}$

With each iteration, we get a better approximation.

Note:  $\varepsilon_i$  is the ionisation energy of the  $i$ -th electron, assuming the other electrons do not change.

$$\varepsilon_i = \int d^3\vec{r} \left( -\frac{\hbar^2}{2m} |\nabla \varphi_i|^2 - \frac{Ze^2}{r} |\varphi_i|^2 \right) + \sum_{j \neq i} \int d^3r_i \int d^3r_j |\varphi_i|^2 |\varphi_j|^2 \frac{e^2}{|r_i - r_j|}$$

### 3.4 Hartree-Fock approximation

In this approximation, we take the antisymmetry property into account:

$$\Psi(1, \dots, N) = \frac{1}{\sqrt{N!}} \left| \begin{pmatrix} \varphi_1(1) & \cdots & \varphi_N(1) \\ \vdots & \ddots & \vdots \\ \varphi_1(N) & \cdots & \varphi_N(N) \end{pmatrix} \right|$$

This then leads to changes:

$$\begin{aligned} \langle H \rangle &= \sum_I \int d^3 \vec{r}_i \left( \varphi_i^*(r_i) \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r_i} \right) \varphi_i(r_i) \right) \\ &+ \frac{1}{2} \sum_{i \neq j} \int d^3 \vec{r}_i \int d^3 \vec{r}_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \left( \underbrace{\varphi_i^*(\vec{r}_i) \varphi_j^*(\vec{r}_j) \varphi_i(\vec{r}_i) \varphi_j(\vec{r}_j)}_{\text{same as before}} - \underbrace{\varphi_i^*(\vec{r}_i) \varphi_j^*(\vec{r}_j) \varphi_i(\vec{r}_j) \varphi_j(\vec{r}_i)}_{\text{exchange term}} \right) \end{aligned}$$

To understand the exchange term, we consider  $N = 2$ :

$$\Psi(1, 2) = \frac{1}{\sqrt{2!}} (\varphi_1(1)\varphi_2(2) - \varphi_1(2)\varphi_2(1))$$

We then plug this into the equation:

$$\begin{aligned} \left\langle \Psi \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Psi \right\rangle &= \frac{1}{2!} \int d^3 r_1 \int d^3 r_2 \left( \varphi_1^*(1)\varphi_2^*(2)\varphi_1(1)\varphi_2(2) + \underbrace{\varphi_1^*(2)\varphi_2^*(1)\varphi_1(2)\varphi_2(1)}_{\vec{r}_1 \leftrightarrow \vec{r}_2: \text{ the same}} \right. \\ &\quad \left. - \varphi_1^*(1)\varphi_2^*(2)\varphi_1(2)\varphi_2(1) - \varphi_1^*(2)\varphi_2^*(1)\varphi_1(1)\varphi_2(2) \right) \end{aligned}$$

From this place on, one has to continue as in the Hartree approximation. The difference is roughly 10%.

### 3.5 The periodic table and Hund's rules

Hartree(-Fock) gives us the result that the electrons are in the field of the nucleus and the other electrons. The other electrons, to some extent, shield the nucleus. So the  $i$ -th electron lives in an effective potential given by the nucleus and all the other electrons. The effective potential  $V_{eff}$  is still spherically symmetric, so the wave function of the  $i$ -th electron will have the following form:

$$\Psi_i = \underbrace{R_{nl}(r_i)}_{\text{radial part}} \underbrace{Y_l^{m_l}(\theta, \varphi)}_{\text{angular part: } l = 0, \dots, n-1} \underbrace{\chi_{m_s}}_{\text{spin}}$$

The general rules for the electrons are:

- $n$  smaller  $\rightarrow E$  smaller (stronger binding)
- $l$  smaller  $\rightarrow E$  smaller (electrons closer to nucleus  $\rightarrow$  stronger binding)
- Those two things compete to some extent.

For each  $n$ , we have a name:

$l =$	0,	1,	2,	3,	...	$n - 1$
name	s	p	d	f	...	
degeneracy	2	6	10	14	$2 \cdot (2l + 1)$	

There are the following shells to surround the nucleus with electrons:

K shell	$n = 1$	$l = 0$	2 elements	H, He	(1s)
L shell	$n = 2$	$l = 0$	2 elements	Li, Be	(2s)
		$l = 1$	6 elements	B,...,Ne	(2p)
M shell	$n = 3$	$l = 0$	2 elements	Na, Mg	(3s)
		$l = 1$	6 elements	Al,...Ar	(3p)
N shell	$n = 4$	$l = 0$	2 elements	K, Ca	(4s)
		$l = 2$	10 elements	Sc,...Zn	(3d)
		$l = 1$	6 elements	Ga,...,Kr	(4p)

The configuration of the electrons defines the chemical properties of the elements. If a shell is completely filled, we have an inert gas.

What is the configuration of the total spin  $S$ , the total orbital angular momentum  $L$ , and the total angular momentum  $\vec{J}$  of the electrons? Here we get Hund's rules. Hund's rules are empirical rules, there are examples where they fail.

Example Carbon (C:  $Z = 6$ ):

In carbon we have:  $(1s)^2(2s)^2(2p)^2$

Each of the  $(2p)$ -electrons can have  $m_l = -1, 0, +1$ ,  $m_s = -\frac{1}{2}, +\frac{1}{2} \rightarrow 6$  possibilities. This then gives in total  $15 = \frac{1}{2}6 \cdot 5$  possibilities:

$L$	$S$	$J$	$(2S+1)L_J$	deg
0	0	0	$^1S_0$	1
1	1	0,1,2	$^3P_0, ^3P_1, ^3P_2$	1,3,5
2	0	2	$^1D_2$	5

The total degeneracy is 15.

For  $L$ , 0 and 2 are symmetric, 1 is antisymmetric. In order for the whole state to be antisymmetric, for  $L = 0, 2$ ,  $S$  has to be antisymmetric, therefore  $S = 0$ . If  $L = 1$ , is antisymmetric, then  $S$  has to be symmetric, therefore  $S = 1$ .

Which one is the ground state?

Rules we use:

- $S$  maximal  
 $S$  large, spin wave function more symmetric  $\rightarrow$  space wave function less symmetric/more antisymmetric  $\rightarrow$  wave function overlap (of electrons) minimal, therefore we have minimal repulsion.  
 For our case:  $S = 1$  (for C)
- $L$  maximal  
 This is the case because for large  $L$ , the electrons are further away from the nucleus, hence further away from each other. Therefore we have less repulsion.  
 For our case:  $L = 1$  (for C), but that is already defined by  $S$ , so this rule does not help us.
- $\Delta E_{SO} = \underbrace{\text{cst.}}_{(J(J+1) - L(L+1) - S(S+1))}$   
 $\left\{ \begin{array}{l} \text{cst} > 0 \text{ if the shell is no more than half filled} \rightarrow J = |L - S| \\ \text{cst} < 0 \text{ if shell more than half filled} \rightarrow J = |L + S| \end{array} \right.$

This comes from the fact that  $V \sim \text{cst} \cdot \vec{L} \cdot \vec{S}$

In our case we therefore want that  $J = 0$ . Our ground state is therefore  $^3P_0$



END