1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. **ELECTRONIC STRUCTURE OF ATOMS**
    - **5.1 The central field approximation and the Periodic Table**
    - 5.2 Consequences of the Indistinguishability of Electrons and the Electron Spin
    - 5.3 Coupling of Angular Momenta
        - 5.3.1 Spin-Orbit Coupling
        - 5.3.2 How to Represent the Eigenfunctions for a System in which two Angular Momenta are Coupled?
    - 5.4 Electronic States of Atoms, Term Symbols, The Ground States of Atoms, Hund's Rules
    - 5.5 Atomic Spectra of Light Atoms, e.g., Na

ELECTRONIC STRUCTURE OF ATOMS

The many-electron atom problem:

The Hamiltonian for an N-electron atom

$$\mathcal{H} = \frac{-\hbar^2}{2m_{nuc}}\nabla^2_{nuc} - \frac{\hbar^2}{2m_e}\left(\nabla^2_{elec_1} + \nabla^2_{elec_2} + \cdots + \nabla^2_{elec_N}\right) + V(nuc, elec_1, elec_2, \cdots elec_N)$$

where all coordinates are with respect to an arbitrarily chosen origin such as the corner of the laboratory room.

First, separate out the translational motion.

$$\mathcal{H} = \mathcal{H}_{transl} + \mathcal{H}_{\substack{internal\\motion}}$$

where

$$\mathcal{H}_{transl} = \frac{-\hbar^2}{2(m_{nuc} + Nm_e)}\nabla^2_{CM}$$

$$\frac{\partial^2}{\partial x_3^2} + \frac{\partial^2}{\partial y_3^2} + \frac{\partial^2}{\partial z_3^2}$$

where x_3, y_3, z_3 is relative to nucleus as ORIGIN

$$\mathcal{H}_{\substack{internal\\motion}} = \frac{-\hbar^2}{2\mu}\left(\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \cdots + \nabla_N^2\right) + V(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N)$$

$$\text{and total wavefunction} = \underbrace{F(X_{CM})\cdot G(Y_{CM})\cdot Q(Z_{CM})}_{\text{describes translational motion of center of mass with respect to corner of lab}}\cdot\underbrace{\Psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N)}_{\text{describes internal motion of electrons relative to nucleus as origin}}$$

Now we need to solve

$$\mathcal{H}_{\substack{internal\\motion}}\Psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) = E\,\Psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N)$$

write out all of $V(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N)$: vector position

$$\mathcal{H}_{\substack{\text{internal}\\ \text{motion}}} = -\frac{\hbar^2}{2\mu}\left(\nabla_1^2 + \nabla_2^2 + \cdots + \nabla_N^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{Ze^2}{r_3} \cdots - \frac{Ze^2}{r_N}$$

$$+ \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} + \cdots$$

$$\mathcal{H}_{\substack{\text{internal}\\ \text{motion}}} = \sum_{i=1}^{N} \underbrace{\left\{ -\frac{\hbar^2}{2\mu}\nabla_i^2 - \frac{Ze^2}{r_i} \right\}}_{\substack{\text{the Hamiltonian of one electron in the Coulomb} \\ \text{field of a positive } (+Ze) \text{ charge at the nucleus,} \\ \text{a central field} \\ \text{i.e. the Hydrogen-like atom}}} + \sum_{\substack{i,j\\ i>j}}\sum \frac{e^2}{r_{ij}}$$

NO LONGER a CENTRAL FIELD PROBLEM

This part is completely separable into N little problems each one is a hydrogen-like atom

Use the 'central field approximation':

That is, replace $V(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) = \sum_{i=1}^{N} -\frac{Ze^2}{r_i} + \sum_{\substack{i,j\\ i>j}}\sum \frac{e^2}{r_{ij}}$

with $\sum_{i=1}^{N} V(r_i)$

where $V(r_3)$ includes integrals over the electron distributions of electrons 1, 2, 4, 5, 6, … N, since it is the potential energy of electron 3 in the field of the nucleus <u>and</u> the electron charge distribution of all the other electrons

$$\mathcal{H}_{\substack{\text{internal}\\ \text{motion}}} \overset{\text{approx.}}{\simeq} \mathcal{H}_{\substack{\text{central}\\ \text{field}}}$$

$$\mathcal{H}_{\substack{\text{central}\\ \text{field}}} = \sum_{i=1}^{N}\left\{\frac{-\hbar^2}{2m}\nabla_i^2 - \underbrace{V(r_i)}\right\}$$

is completely separable into N little problems, each one of which can be solved only when all the others are also solved.

potential energy of the ith electron in the central field created by the $+Ze$ of the nucleus and the total charge distribution of all the other $(N-1)$ electrons

Solutions are product functions, each one looks like $\psi(r_3, \theta_3, \phi_3) = F(r_3) \cdot Y_{lm}(\theta_3, \phi_3)$ **an 'orbital'**

found by solving $\left(\frac{-\hbar^2}{2m}\underbrace{\nabla_3^2} - V(r_3)\right)\psi(r_3, \theta_3, \phi_3) = \epsilon\psi(r_3, \theta_3, \phi_3)$

$$\left\{\frac{1}{r_3}\frac{\partial^2}{\partial r_3^2} r_3 + \frac{1}{r_3^2\sin\theta_3}\frac{\partial}{\partial\theta_3}\sin\theta_3\frac{\partial}{\partial\theta_3} + \frac{1}{r_3^2\sin^2\theta_3}\frac{\partial^2}{\partial\phi_3^2}\right\}$$

We have solved this before, separating out ϕ_3, then θ_3 parts, with results $Y_{lm}(\theta_3, \phi_3)$, leaving the last part,

$$\frac{\left\{\frac{-\hbar^2}{2m}\frac{1}{r_3}\frac{\partial^2}{\partial r_3^2} r_3 + \frac{l_3(l_3+1)\hbar^2}{2m r_3^2} - \underset{\sim}{V(r_3)}\right\} F(r_3)}{F(r_3)} = \epsilon$$

This radial equation has to be solved at the same time as all the other radial equations for $(N-1)$ electrons in $r_1, r_2, r_4, r_5, \ldots r_N$ since $V(r_3)$ contains in it integrals over $\psi^*\psi(r_1, \theta_1, \phi_1)$, $\psi^*\psi(r_2, \theta_2, \phi_2)$, etc.

SELF-CONSISTENT FIELD

The self-consistent field therefore leads to a total wavefunction for all N electrons which can be written in terms of simple products of <u>one-electron</u> functions ('orbitals')

such as $\psi_{100}(1)\cdot\psi_{100}(2)\cdot\psi_{200}(3)\cdot\psi_{200}(4)$ **$1s^2 2s^2$**

or $\psi_{100}(1)\cdot\psi_{100}(2)\cdot\psi_{210}(3)\,\psi_{531}(4)$ or whatever **$1s^2 2p_0 5f_1$**

n l m quantum numbers just as in the true hydrogen-like atom with only one electron

$Y_{l,m_i}(\theta_i,\phi_i)$ angular momentum functions just as in the true hydrogen-like atom with only one electron

However, the $F(r_i)$ can be very complicated and is <u>not the same</u> as the hydrogen-like $R_{nl}(r)$. Also $F(r_i)$ has to be solved for each **configuration**, that is, for each product function. $F(r_1)$ in **$1s^2 2s^2$** is different from the $F(r_1)$ in **$1s^2 2p_0 5f_1$**.

The intrinsic ('spin') angular momentum of an electron imposes conditions on how many of the N electrons in an atom are permitted to have the same $F_{n_i l_i}(r_i)\cdot Y_{l_i m_i}(\theta_i,\phi_i)$ function.

A many-electron atom

Using the ***central field approximation***:

$$V \approx V(r_1) + V(r_2) + V(r_3) + \ldots$$

no matter how complex a numerical or functional form each $V(r_i)$ may have.

It follows that,

$$\mathcal{H}(1, 2, \ldots) \approx \mathcal{H}(1) + \mathcal{H}(2) + \mathcal{H}(3) + \ldots$$

where

$$\mathcal{H}(1) = -(\hbar^2/2\mu)\, \nabla_1^{\,2} + V(r_1)$$

which results in solutions of the type

$$\Psi(1) = F_\ell\,(r_1) \bullet Y_{\ell m}(\theta_1, \phi_1)$$

an “orbital”, a one-electron function and $\varepsilon(1)$

but $F_\ell\,(r_1)$ is not necessarily of the form $R_{n\ell}(r_1)$ and $\varepsilon(1)$ is not of the form $-(Z^2/n^2)(e^2/2a_0)$ since $V(r_1)$ is not of the form $-Ze^2/r_1$.

Consequences of separability and central field approximation:

Permits use of the following :

- for each electron an “atomic orbital”:

  quantum numbers ℓ and m_ℓ

  and the functions $Y_{\ell m}(\theta_1,\phi_1)$.

- for the whole atom a product of atomic orbitals (one-electron functions):

$$\Psi(1,2,3,4,\ldots) = \Psi(1) \bullet \Psi(2) \bullet \Psi(3) \bullet \ldots$$

  and the energy eigenvalue a sum of orbital energies

$$E_{\text{total}} = \sum_i \varepsilon(i)$$

But correlation of electronic motions is left out.

More drastic approximations permit simple calculations.

a) Use an effective charge for each electron
That is, replace $V(r_3)$ by $-\frac{Z_{eff}(3)\, e^2}{r_3}$

Each $Z_{eff}(i)$ is different and a set of $Z_{eff}(i)$ is only good for a given electronic configuration. See table of values by Clementi + Raimondi.

b) Use an effective charge for each electron
That is, replace $V(r_3)$ by $-Z_{eff}(3)\frac{e^2}{r_3}$
For a given electronic configuration, obtain an approximate $Z_{eff}(i)$ for each electron by using one simple set of rules (Slater's rules) and further simplify the form of $R_{nl}(r)$.

Use of an effective charge for each electron leads to

$$\mathcal{H}_{\text{internal motion}} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2\mu}\nabla_i^2 - Z_{eff}(i)\frac{e^2}{r_i} \right\}$$

which has the virtue of being exactly separable into hydrogen-like one-electron Schrödinger equations, which we have already solved, with energies given by $\epsilon_i = -\left[\frac{Z_{eff}(i)}{n_i}\right]^2 \frac{e^2}{2a}$

$$E_{\text{electronic}} = \sum_{i=1}^{N} -\left(\frac{Z_{eff}(i)}{n_i}\right)^2 \frac{e^2}{2a}$$

and functions

$$\psi(r_i, \theta_i, \phi_i) = R_{n_i l_i}(r_i) \cdot Y_{l_i m_i}(\theta_i, \phi_i)$$

where Z is replaced by $Z_{eff}(i)$ in the same radial functions of H atom.

Table 4.9 *Best values of ζ for the ground state of neutral atoms*[a]

$\zeta = \frac{Z_{eff}}{n}$

	Z	1s	2s	2p	3s	3p	4s	3d	4p
He	2	1.6875							
Li	3	2.6906	0.6396						
Be	4	3.6848	0.9560						
B	5	4.6795	1.2881	1.2107					
C	6	5.6727	1.6083	1.5679					
N	7	6.6651	1.9237	1.9170					
O	8	7.6579	2.2458	2.2266					
F	9	8.6501	2.5638	2.5500					
Ne	10	9.6421	2.8792	2.8792					
Na	11	10.6259	3.2857	3.4009	0.8358				
Mg	12	11.6089	3.6960	3.9129	1.1025				
Al	13	12.5910	4.1068	4.4817	1.3724	1.3552			
Si	14	13.5745	4.5100	4.9725	1.6344	1.4284			
P	15	14.5578	4.9125	5.4806	1.8806	1.6288			
S	16	15.5409	5.3144	5.9885	2.1223	1.8273			
Cl	17	16.5239	5.7152	6.4966	2.3561	2.0387			
Ar	18	17.5075	6.1152	7.0041	2.5856	2.2547			
K	19	18.4895	6.5031	7.5136	2.8933	2.5752	0.8738		
Ca	20	19.4730	6.8882	8.0207	3.2005	2.8861	1.0995		
Sc	21	20.4566	7.2868	8.5273	3.4466	3.1354	1.1581	2.3733	
Ti	22	21.4409	7.6883	9.0324	3.6777	3.3679	1.2042	2.7138	
V	23	22.4256	8.0907	9.5364	3.9031	3.5950	1.2453	2.9943	
Cr	24	23.4138	8.4919	10.0376	4.1226	3.8220	1.2833	3.2522	
Mn	25	24.3957	8.8969	10.5420	4.3393	4.0364	1.3208	3.5094	
Fe	26	25.3810	9.2995	11.0444	4.5587	4.2593	1.3585	3.7266	
Co	27	26.3668	9.7025	11.5462	4.7741	4.4782	1.3941	3.9518	
Ni	28	27.3526	10.1063	12.0476	4.9870	4.6950	1.4277	4.1765	
Cu	29	28.3386	10.5099	12.5485	5.1981	4.9102	1.4606	4.4002	
Zn	30	29.3245	10.9140	13.0490	5.4064	5.1231	1.4913	4.6261	
Ga	31	30.3094	11.2995	13.5454	5.6654	5.4012	1.7667	5.0311	1.5554
Ge	32	31.2937	11.6824	14.0411	5.9299	5.6712	2.0109	5.4171	1.6951
As	33	32.2783	12.0635	14.5368	6.1985	5.9499	2.2360	5.7928	1.8623
Se	34	33.2622	12.4442	15.0326	6.4678	6.2350	2.4394	6.1590	2.0718
Br	35	34.2471	12.8217	15.5282	6.7395	6.5236	2.6382	6.5197	2.2570
Kr	36	35.2316	13.1990	16.0235	7.0109	6.8114	2.8289	6.8753	2.4423

[a] E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963); computed for ground state configuration, except for Cr([Ar]$4s^2 3d^4$) and Cu([Ar]$4s^2 3d^9$).

$$Z_{eff}(i) = \underset{\substack{\nearrow \\ \text{true number} \\ \text{of protons} \\ \text{in nucleus}}}{Z} - \underset{\substack{\uparrow \\ \text{screening} \\ \text{constant} \\ \text{for the} \\ i^{th}\text{ electron}}}{s_i}$$

Clementi - Raimondi rules for atoms from He through Kr. The equations obtained by Clementi and Raimondi are

$$\begin{aligned}
s_{1s} &= 0.3[N(1s) - 1] + 0.0072[N(2s) + N(2p)] \\
&\quad + 0.0158[N(3s) + N(3p) + N(4s) + N(3d) + N(4p)] \\
s_{2s} &= 1.7208 + 0.3601[N(2s) + N(2p) - 1] \\
&\quad + 0.2062[N(3s) + N(3p) + N(4s) + N(3d) + N(4p)] \\
s_{2p} &= 2.5787 + 0.3326[N(2p) - 1] - 0.0773N(3s) \\
&\quad - 0.0161[N(3p) + N(4s)] - 0.0048N(3d) + 0.0085N(4p) \\
s_{3s} &= 8.4927 + 0.2501[N(3s) + N(3p) - 1] + 0.0778N(4s) \\
&\quad + 0.3382N(3d) + 0.1978N(4p). \\
s_{3p} &= 9.3345 + 0.3803[N(3p) - 1] + 0.0526N(4s) \\
&\quad + 0.3289N(3d) + 0.1558N(4p) \\
s_{4s} &= 15.505 + 0.0971[N(4s) - 1] + 0.8433N(3d) \\
&\quad + 0.0687N(4p) \\
s_{3d} &= 13.5894 + 0.2693[N(3d) - 1] - 0.1065N(4p) \\
s_{4p} &= 24.7782 + 0.2905[N(4p) - 1]
\end{aligned}$$

$$Z_{eff}(i) = \underset{\substack{\uparrow \\ \text{true} \\ \text{number} \\ \text{of protons} \\ \text{in nucleus}}}{Z} - \underset{\substack{\uparrow \\ \text{screening} \\ \text{constant} \\ \text{for the} \\ i^{th}\ \text{electron}}}{s_i}$$

Slater's rules:

1. $s_{1s} = 0.30$

2. For electrons with $n > 1$ and $\ell = 0, 1$

$$s_{n\ell} = 0.35k_{same} + 0.85k_{in} + 1.00k_{inner}$$

where

k_{same} = number of other electrons in the same shell as the screened electron of interest

k_{in} = number of electrons in the shell with principal quantum number n-1

k_{inner} = number of electrons in the shell with principal quantum number n-2

3. For 3d electrons

$$s_{3d} = 0.35k_{3d} + 1.00k_{in}$$

where

k_{3d} = number of 3d electrons

k_{in} = number of electrons with $n \leq 3$ and $\ell < 2$

$$\langle r^2 \rangle = \int_0^\infty R_{nl}(r)^* r^2 R_{nl}(r)\, r^2 dr$$ for a hydrogen-like atom

$$= \frac{n^2}{2Z^2}\left[5n^2 + 1 - 3l(l+1)\right] a_0^2$$

$$= \frac{1^2}{2Z^2}\left[5 \cdot 1^2 + 1 - 0\right] a_0^2 = \frac{3}{Z^2} a_0^2$$ for ground state

$$\alpha \approx \frac{4a_0^3}{Z^4}$$ Exact answer is $\left(\frac{9}{2}\right)\frac{a_0^3}{Z^4}$

if use ionization energy as $\overline{\Delta E}$, i.e. $\overline{\Delta E} \approx \frac{Z^2}{n^2}\frac{e^2}{2a_0}$

For many-electron atoms, need to sum $\langle r^2 \rangle_i$ for each electron over all the electrons in the atom. $\zeta_i \equiv (Z_i/n_i)$ Z_i' = effective charge for the ith electron

$$\langle r^2 \rangle_i \approx (2n_i + 2)(2n_i + 1)\frac{a_0^2}{4\zeta_i^2}$$

$$E_i \approx -\zeta_i^2 \frac{e^2}{2a_0}$$

$$\overline{\Delta E}_i \approx \zeta_i^2 \frac{e^2}{2a_0}$$

$$\alpha \approx \frac{2}{3} e^2 \sum_i \frac{\langle r^2 \rangle_i}{(\overline{\Delta E})_i} \approx \sum_i^{\text{all electrons}} \frac{(2n_i+2)(2n_i+1)\, a_0^3}{\zeta_i^4}$$

$$\left\{ \begin{array}{l} R_{n_i l_i}(r_i) \approx \left[\dfrac{(2\zeta_i/a_0)^{2n_i+1}}{(2n_i)!}\right]^{1/2} r_i^{\,n_i - 1} e^{-\zeta_i \frac{r_i}{a_0}} \quad \text{Slater-type atomic orbitals} \\ \Theta_{l_i m_i}(\theta) \cdot \Phi_{m_i}(\phi) \quad \text{spherical harmonics for the ith electron} \end{array} \right.$$

first ionization energy minimum energy required to remove an electron from the neutral gaseous atom (or molecule)

Ca^+ from Ca 589.81 kJ/mol
Ca^{2+} from Ca 1734.80 kJ/mol

$\underline{Ca^{2+}_{(g)} + e-}$ $E(Ca^{2+})$

$IE_2 = 1145.0$ kJ/mol

↑ $\underline{Ca^{+}_{(g)} + e-}$ $E(Ca^{+})$

$IE_1 = 589.81$ kJ/mol

E $\underline{\quad Ca_{(g)}\quad}$ $E(Ca)$

$IE_1 = E(Ca^+) - E(Ca)$
$IE_2 = E(Ca^{2+}) - E(Ca^+)$

electron affinity energy released when an electron is added to an atom or molecule

$Cl_{(g)} + e^-$ E(Cl)
↑

E $Cl^-_{(g)}$ E(Cl^-)

$EA = E(Cl) - E(Cl^-)$.

EA is positive or negative,
depending on which is lower in energy,
the neutral atom or the negative ion:

Note that the definitions of *IE* and *EA* appear to be opposite,

$$IE_1 \equiv E(+ion) - E(neutral)$$

$$EA \equiv E(neutral) - E(- ion)$$

but the energy change is associated with electron detachment process in both cases, *with the energy difference IE and EA being defined for the neutral atom*

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Two more complications that arise are

- ***the indistinguishability of electrons***
- ***the electron spin***.

These are intimately connected.

Let us proceed at two levels:

Level I: Electrons have spin and are indistinguishable but we neglect coupling of angular momenta (spin-orbit coupling)

Level II: Include spin-orbit coupling

Fundamental particles have intrinsic angular momentum ("spin").

Examples:
s=½ for electrons, neutrons and protons.
I = 1 for deuteron, I = ½ for ^{19}F nucleus,
I =3/2 for ^{35}Cl nucleus.

fermions =	particles with half-integer spins obey Fermi-Dirac statistics
bosons =	particles with integer (and 0) spins obey Bose-Einstein statistics

Pauli exclusion principle states:

The total wavefunction of a physical system must be ***ANTISYMMETRIC*** with respect to interchange of any two indistinguishable ***fermions*** <u>and</u> also ***SYMMETRIC*** with respect to interchange of any two indistinguishable ***bosons***.

Consequences of indistinguishability of particles in a system:

Example, non-interacting indistinguishable particles of mass M live on a circle of radius R:

$$\mathcal{H}(1, 2, \ldots) = \mathcal{H}(1) + \mathcal{H}(2) + \mathcal{H}(3) + \ldots$$

where $\mathcal{H}(1) = -(\hbar^2/2MR^2)\,(\partial^2/\partial\phi_1{}^2)$ solutions are

$\Phi_{k1}(1) = (2\pi)^{-\frac{1}{2}} \exp[ik_1\phi_1]$ where $k_1 = 0, \pm 1, \ldots$

$$\varepsilon(1) = k_1{}^2\hbar^2/2MR^2$$

so that for the system,

$$\Psi(1,2,3,4,\ldots) = \Phi_{k1}(1) \bullet \Phi_{k2}(2) \bullet \Phi_{k3}(3) \bullet \ldots$$

$$E = \textstyle\sum_i k_i{}^2\hbar^2/2MR^2$$

Indistinguishability means that for the state where the quantum numbers are 0,-1,2,-3 and the energy is $\hbar^2/2MR^2\,(0^2+1^2+2^2+3^2)$,

$\Psi(1,2,3,4) = \Phi_0(1) \bullet \Phi_{-1}(2) \bullet \Phi_2(3) \bullet \Phi_{-3}(4)$ is not distinguishable from

$$\Psi(1,2,3,4) = \Phi_0(2) \bullet \Phi_{-1}(1) \bullet \Phi_2(3) \bullet \Phi_{-3}(4)$$

$$\Psi(1,2,3,4) = \Phi_0(4) \bullet \Phi_{-1}(3) \bullet \Phi_2(1) \bullet \Phi_{-3}(2)$$

or any of the other 4! possibilities.
Since these functions are indistinguishable from each other, we must use a linear combination of 4! functions in order to have a complete description that includes ***indistinguishability of the particles***.

Since each one is individually normalized and all possibilities are equally likely, the linear combination has to be of the form:

$$\Psi^{p}(1,2,3,4) =$$
$$(4!)^{-1/2}\{\textstyle\sum_{ij} \pm\mathcal{P}_{ij}\, \Phi_0(1)\bullet \Phi_{-1}(2)\bullet\Phi_2(3)\bullet\Phi_{-3}(4)\}$$

where $\mathcal{P}_{ij}$ is the permutation operator.

± indicates that each term after permutation will have a coefficient that is either +1 or -1.

The specific linear combination with a specific set of coefficients is labeled here with ^{p}.

Consequences of the particles being fermions

$$\mathcal{P}_{13}\,\Psi^{p}(1,2,3,4) = -\Psi^{p}(1,2,3,4)$$

$$\mathcal{P}_{23}\,\Psi^{p}(1,2,3,4) = -\Psi^{p}(1,2,3,4)$$

and so on, for any and all such permutations!

Consequences of the particles being bosons

$$\mathcal{P}_{13}\,\Psi^{p}(1,2,3,4) = +\Psi^{p}(1,2,3,4)$$

$$\mathcal{P}_{23}\,\Psi^{p}(1,2,3,4) = +\Psi^{p}(1,2,3,4)$$

and so on, for any and all such permutations!

Use a determinant to ensure these consequences for fermions

Let columns designate Φ_0 , Φ_{-1} , Φ_2 , Φ_{-3} and rows designate the fermions 1,2,3,4

$\Psi^p(1,2,3,4)$ =

$(4!)^{-1/2}$ det | $\Phi_0(1)$ $\Phi_{-1}(2)$ $\Phi_2(3)$ $\Phi_{-3}(4)$ |

where det | $\Phi_0(1)$ $\Phi_{-1}(2)$ $\Phi_2(3)$ $\Phi_{-3}(4)$ | means

$$\begin{vmatrix} \Phi_0(1) & \Phi_{-1}(1) & \Phi_2(1) & \Phi_{-3}(1) \\ \Phi_0(2) & \Phi_{-1}(2) & \Phi_2(2) & \Phi_{-3}(2) \\ \Phi_0(3) & \Phi_{-1}(3) & \Phi_2(3) & \Phi_{-3}(3) \\ \Phi_0(4) & \Phi_{-1}(4) & \Phi_2(4) & \Phi_{-3}(4) \end{vmatrix}$$

Why a determinant?

- value of det is unchanged if rows are interchanged with columns
- value of det *changes sign* if any two rows (or columns) are *interchanged with each other*
- det = 0 if all elements of one row (or column) are identical with or multiples of the corresponding elements of another row.

Recall how to expand a determinant

$$\begin{vmatrix} f(1) & g(1) & h(1) \\ f(2) & g(2) & h(2) \\ f(3) & g(3) & h(3) \end{vmatrix}$$

in terms of the elements of row 1, e.g.,

$$= (-1)^{1+1} f(1) \times \begin{vmatrix} g(2) & h(2) \\ g(3) & h(3) \end{vmatrix}$$

$$+ (-1)^{1+2} g(1) \times \begin{vmatrix} f(2) & h(2) \\ f(3) & h(3) \end{vmatrix}$$

$$+ (-1)^{1+3} h(1) \times \begin{vmatrix} f(2) & g(2) \\ f(3) & g(3) \end{vmatrix}$$

$$= f(1)g(2)h(3) - f(1)h(2)g(3) - g(1)f(2)h(3)$$
$$+ g(1)h(2)f(3) + h(1)f(2)g(3) - h(1)g(2)f(3)$$

The normalized wavefunction $\Psi(1,2,3)$ is

$$(3!)^{-1/2}\{ f(1)g(2)h(3) - f(1)h(2)g(3) - g(1)f(2)h(3)$$
$$+ g(1)h(2)f(3) + h(1)f(2)g(3) - h(1)g(2)f(3)\}$$

Verify for yourself that $\mathcal{P}_{12}\Psi(1,2,3) = -\Psi(1,2,3)$

In general, we can represent the entire ***antisymmetrized function*** that results from expanding the determinant as

$(N!)^{-1/2}\sum(-1)^p\mathcal{P}\ f(1)g(2)h(3)\cdots z(N)$

The operator $(N!)^{-1/2}\sum(-1)^p\mathcal{P}$ is called the antisymmetrization operator, where p is the number of two-fold permutations, $\mathcal{P}$ is the permutation operator which is a sequence of two-fold permutations.

f(1) is a ***spin-orbital***, that is, a product of a space function and a spin function, e.g., $f(1) = 1s\alpha(1)$

A determinant automatically satisfies Pauli exclusion principle for fermions.

For the electronic configuration $1s^2$ for ground state of a He atom

$$\Psi^p(1,2) = (2!)^{-1/2} \det |\, \Phi_{1s\alpha}(1)\ \ \Phi_{1s\beta}(2)\, |$$

For the electronic configuration $1s^2 2s^2$ for the ground state of a Be atom

$$\Psi^p(1,2,3,4) =$$

$$(4!)^{-1/2} \det |\, \Phi_{1s\alpha}(1)\ \ \Phi_{1s\beta}(2)\ \ \Phi_{2s\alpha}(3)\ \ \Phi_{2s\beta}(4)\, |$$

Let us examine term by term for He atom:

$$(2!)^{-1/2} \begin{vmatrix} \Phi_{1s\alpha}(1) & \Phi_{1s\beta}(1) \\ \Phi_{1s\alpha}(2) & \Phi_{1s\beta}(2) \end{vmatrix}$$

$$= (2!)^{-1/2} \left\{ \Phi_{1s\alpha}(1)\bullet\Phi_{1s\beta}(2) - \Phi_{1s\beta}(1)\bullet\Phi_{1s\alpha}(2) \right\}$$

$$= \underbrace{\Phi_{1s}(1)\bullet\Phi_{1s}(2)}_{\text{space}} \times \underbrace{(2!)^{-1/2} \left\{ \alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2) \right\}}_{\text{spin}}$$

antisymmetric:

$$\mathcal{P}_{12}\, \Phi_{1s}(1)\bullet\Phi_{1s}(2)\times(2!)^{-1/2}\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}$$

$$= \Phi_{1s}(2)\bullet\Phi_{1s}(1)\times(2!)^{-1/2}\{\alpha(2)\bullet\beta(1) - \beta(2)\bullet\alpha(1)\}$$

$$= \underset{\nwarrow}{-}\, \Phi_{1s}(1)\bullet\Phi_{1s}(2)\times(2!)^{-1/2}\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}$$

Let us examine term by term for He atom excited state 1s2s. This could be $1s\alpha 2s\alpha$ or $1s\beta 2s\beta$ or $1s\alpha 2s\beta$ or $1s\beta 2s\alpha$. Each one has a different determinant.

$1s\alpha 2s\alpha$ stands for the function D_1

$$(2!)^{-1/2} \begin{vmatrix} \Phi_{1s\alpha}(1) & \Phi_{2s\alpha}(1) \\ \Phi_{1s\alpha}(2) & \Phi_{2s\alpha}(2) \end{vmatrix}$$

$$= (2!)^{-1/2}\{\Phi_{1s\alpha}(1)\bullet\Phi_{2s\alpha}(2) - \Phi_{2s\alpha}(1)\bullet\Phi_{1s\alpha}(2)\}$$

$$=(2!)^{-1/2}\underbrace{\{\Phi_{1s}(1)\bullet\Phi_{2s}(2)-\Phi_{2s}(1)\bullet\Phi_{1s}(2)\}}_{\text{space}}\times\underbrace{\alpha(1)\bullet\alpha(2)}_{\text{spin}}$$

Similarly

$$D_2 = (2!)^{-\frac{1}{2}} \begin{vmatrix} \Phi_{1s\beta}(1) & \Phi_{2s\beta}(1) \\ \Phi_{1s\beta}(2) & \Phi_{2s\beta}(2) \end{vmatrix}$$

$$=(2!)^{-\frac{1}{2}}\underbrace{\{\Phi_{1s}(1)\bullet\Phi_{2s}(2)-\Phi_{2s}(1)\bullet\Phi_{1s}(2)\}}_{\text{space}}\times \underbrace{\beta(1)\bullet\beta(2)}_{\text{spin}}$$

$$D_3 = (2!)^{-\frac{1}{2}} \{\Phi_{1s\alpha}(1)\bullet\Phi_{2s\beta}(2) - \Phi_{2s\beta}(1)\bullet\Phi_{1s\alpha}(2)\}$$

and

$$D_4 = (2!)^{-\frac{1}{2}} \{\Phi_{1s\beta}(1)\bullet\Phi_{2s\alpha}(2) - \Phi_{2s\alpha}(1)\bullet\Phi_{1s\beta}(2)\}$$

We need to form linear combinations of D_3 and D_4 in order to be able to factor out space and spin:

$$(2!)^{-\frac{1}{2}} (D_3+D_4) = (2!)^{-\frac{1}{2}}\{\Phi_{1s}(1)\bullet\Phi_{2s}(2) - \Phi_{2s}(1)\bullet\Phi_{1s}(2)\}(2!)^{-\frac{1}{2}}\{\alpha(1)\bullet\beta(2) + \beta(1)\bullet\alpha(2)\}$$

$$(2!)^{-\frac{1}{2}} (D_3-D_4) = (2!)^{-\frac{1}{2}}\{\Phi_{1s}(1)\bullet\Phi_{2s}(2) + \Phi_{2s}(1)\bullet\Phi_{1s}(2)\}(2!)^{-\frac{1}{2}}\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}$$

All four are ***antisymmetric*** with respect to interchange of electrons 1 and 2.

For the 1s2s electronic configuration of helium atom,

D_1, D_2, $(2!)^{-\frac{1}{2}}(D_3+D_4)$ constitute the S=1 state, also called ortho helium
and $(2!)^{-\frac{1}{2}}(D_3-D_4)$ constitutes the S=0 state, also called para helium
These are the eigenfunctions of the operators
$\boldsymbol{S}_{z,\,total}$, $\boldsymbol{S}_{total}^{\;2}$.

In contrast, the ground state, $1s^2$, is S=0 only.

Corollary:
Two electrons assigned the same set (n,ℓ,m_ℓ, m_s) would appear as two identical columns containing the same spin-orbital.
The properties of a determinant guarantee that the value of such a determinant is <u>zero</u>.
In other words, such a state can not exist.

Total wavefunction for an atom:

$$\psi_{\text{translation}}(X_{cm}, Y_{CM}, Z_{cm}) \cdot \underbrace{\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots)}$$

$$\frac{1}{\sqrt{4!}} \Big\{ \psi_{100}(1)\cdot\psi_{100}(2)\cdot\psi_{200}(3)\cdot\psi_{200}(4)\; \alpha(1)\cdot\beta(2)\cdot\alpha(3)\,\beta(4) \;-\; \psi_{100}(2)\cdot\psi_{100}(1)\cdot\psi_{200}(3)\cdot\psi_{200}(4)\; \alpha(2)\cdot\beta(1)\cdot\alpha(3)\cdot\beta(4)$$

$$-\psi_{100}(1)\cdot\psi_{100}(2)\cdot\psi_{200}(4)\cdot\psi_{200}(3)\; \alpha(1)\cdot\beta(2)\cdot\alpha(4)\cdot\beta(3) \;+\; \text{etc.} \quad \text{24 terms in all} \Big\}$$

short-hand for which is $1s^2 2s^2$

"electronic configuration"

Be atom has a 'ground' (lowest energy) configuration $1s^2 2s^2$. All other electronic configurations for Be atom such as $1s^2 2s\, 2p_0$ etc. have higher energy.

The central field approximation permits us to talk about electronic states of atoms in terms of single configurations such as $1s^2 2s^2 2p^4$ for carbon, because the $Y_{lm}(\theta,\phi)$ parts are the same as for a hydrogen-like atom, that is, the quantum numbers l and m have <u>the</u> <u>same</u> significance as for a true one-electron system. However, the quantities ϵ which add together to give the electronic energy in

$$E_{total} = E_{transl} + E_{electronic}$$

can no longer be related to $\frac{1}{n^2}$.

Thus, we can generate the Periodic Table of the elements by
a) how many electrons? (Same as atomic number for a neutral atom)
b) assign $n\,l\,m$ for each, subject to Pauli exclusion principle, using lowest energy orbitals.

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
    - 5.1 The central field approximation and the Periodic Table
    - 5.2 Consequences of the Indistinguishability of Electrons and the Electron Spin
    - **5.3 Coupling of Angular Momenta**
        - **5.3.1 Spin-Orbit Coupling**
        - **5.3.2 How to Represent the Eigenfunctions for a System in which two Angular Momenta are Coupled?**
    - 5.4 Electronic States of Atoms, Term Symbols, The Ground States of Atoms, Hund's Rules
    - 5.5 Atomic Spectra of Light Atoms, e.g., Na

COUPLING OF ANGULAR MOMENTA

What happens when the physical system has more than one angular momentum? Can the TOTAL ANGULAR MOMENTUM be specified?

Consider two sources of angular momentum $\mathbf{J}_1$ and $\mathbf{J}_2$

(Net or Total) angular momentum is the VECTOR SUM

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$$

What are the possible results of the vector sum? Consider an example:

Example:

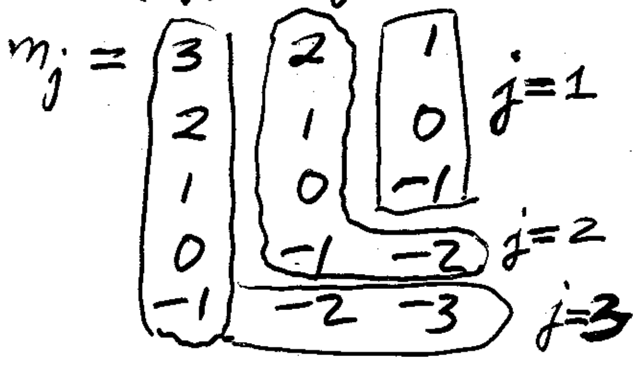
$$j_1 = 2 \qquad m_{j_1} = 2,\ 1,\ 0,\ -1,\ -2$$

$$j_2 = 1 \qquad m_{j_2} = 1,\ 0,\ -1$$

The sum of the z components

$$J_z = J_{1z} + J_{2z}$$

What are the eigenvalues of J_z? $m_j\hbar$ These are the eigenvalues of $J_{1z} + J_{2z}$, which are $(m_{j_1} + m_{j_2})\hbar$. All possible sums are shown:



$$m_j = \begin{array}{ccc} 3 & 2 & 1 \\ 2 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & -2 \\ -1 & -2 & -3 \end{array}$$

Thus the allowed values of j are found to be:

$$j_1 + j_2,\ j_1 + j_2 - 1,\ j_1 + j_2 - 2,\ \ldots\ |j_1 - j_2|$$

The total number of values for m_j must be

$$(2j_1+1)(2j_2+1) = 4j_1j_2 + 2(j_1+j_2)+1$$

The maximum value of m_j must be (j_1+j_2). Using $\mathbf{J}_-$ we should be able to generate the other states, stepping down from (j_1+j_2) to lead to m_j values equal to

$$(j_1+j_2),\ (j_1+j_2-1),\ (j_1+j_2-2),\ \ldots,\ -(j_1+j_2)$$

There are only $2(j_1+j_2)+1$ numbers here. Therefore, there must be others. To get the others:

$$m_j = j_1+j_2-1 \text{ can arise from } \begin{cases} j = j_1+j_2 & \text{and also from} \\ j = j_1+j_2-1 & \end{cases}$$

Therefore $j = j_1+j_2-1$ must be another set of states, and so on.

Since $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$ is an ANGULAR MOMENTUM then,

$$[\mathbf{J}^2, \mathbf{J}_x] = 0 \quad \text{in which } \mathbf{J}_x = \mathbf{J}_{1x} + \mathbf{J}_{2x}$$

$$[\mathbf{J}^2, \mathbf{J}_y] = 0 \quad \mathbf{J}_y = \mathbf{J}_{1y} + \mathbf{J}_{2y}$$

$$[\mathbf{J}^2, \mathbf{J}_z] = 0 \quad \mathbf{J}_z = \mathbf{J}_{1z} + \mathbf{J}_{2z}$$

$$[\mathbf{J}_x, \mathbf{J}_y] = i\hbar \mathbf{J}_z \quad \text{and others in cyclic order}$$

BUT WHAT CAN WE SAY ABOUT COMMUTATION BETWEEN THE SUM AND ONE OF THE VECTORS?

EXAMPLE: "SPIN-ORBIT COUPLING"

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

where $\mathbf{L}$ is ORBITAL ANGULAR MOMENTUM
$\mathbf{S}$ is "SPIN" ANGULAR MOMENTUM

We can easily see that

$$[\mathbf{J}^2, \mathbf{L}^2] = 0 \qquad [\mathbf{J}^2, \mathbf{S}^2] = 0$$

Proof:

$$[(\mathbf{L}+\mathbf{S})^2, \mathbf{L}^2] = [(\mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}), \mathbf{L}^2]$$

$$= [(\mathbf{L}^2 + \mathbf{S}^2 + 2L_xS_x + 2L_yS_y + 2L_zS_z), \mathbf{L}^2]$$

$= 0$ since $[L_x, \mathbf{L}^2] = 0$ etc for all the components of $\mathbf{L}$ and $\mathbf{L}$ and $\mathbf{S}$ commute.

However,

$$[\mathbf{J}^2, L_z] \neq 0 \qquad [\mathbf{J}^2, S_z] \neq 0$$

Proof: As above, this can be rewritten as:

$$[(\mathbf{L}^2 + \mathbf{S}^2 + 2L_xS_x + 2L_yS_y + 2L_zS_z), L_z] = 2[L_x, L_z]S_x + 2[L_y, L_z]S_y$$

$$= 2i\hbar(L_xS_y - L_yS_x)$$

$$\neq 0$$

EIGENFUNCTIONS:

How to represent the eigenfunctions for a system in which two angular momenta are coupled?

- Besides providing j and m_j we need to also give l and s, as in

$$|l, s; j, m_j\rangle$$

where $j = l+s, \ldots, l-s$

$m_j = j, j-1, \ldots, -j$

- The operator equations are (Postulate 2):

$$\mathbf{J}^2 |l, s; j, m_j\rangle = j(j+1)\hbar^2 |l, s; j, m_j\rangle$$
$$\mathbf{L}^2 |l, s; j, m_j\rangle = l(l+1)\hbar^2 |l, s; j, m_j\rangle$$
$$\mathbf{S}^2 |l, s; j, m_j\rangle = s(s+1)\hbar^2 |l, s; j, m_j\rangle$$
$$\mathbf{J}_z |l, s; j, m_j\rangle = m_j\hbar |l, s; j, m_j\rangle$$

and since $\mathbf{J}^2 = (\mathbf{L}+\mathbf{S})^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}$

$$\mathbf{L}\cdot\mathbf{S} |l, s; j, m_j\rangle = \tfrac{1}{2}[j(j+1) - l(l+1) - s(s+1)]\hbar^2 |l, s; j, m_j\rangle$$

- How do we find the eigenfunctions? By expansion in terms of a complete orthonormal set of functions, such as the eigenfunctions of $(\mathbf{L}_z + \mathbf{S}_z)$, which are the <u>product</u> <u>functions</u>

$$\underbrace{|l, m_l\rangle}_{\text{EIGENFUNCTION of } \mathbf{L}_z} \cdot \underbrace{|s, m_s\rangle}_{\text{EIGENFUNCTION of } \mathbf{S}_z}$$

That is, we can write $\Psi = c_1\phi_1 + c_2\phi_2 + \cdots$

$$|l, s; j, m_j\rangle = \sum_{m_l} \sum_{m_s} c_{m_l m_s} \, |l, m_l\rangle \cdot |s, m_s\rangle$$

where the coefficients can be found by the usual method: $\int \phi_1^* \Psi \, d\tau = c_1$

$$\langle l, m_l| \cdot \langle s, m_s | l, s; j, m_j\rangle = c_{m_l m_s}$$

THESE "vector coupling coefficients" or "Clebsch-Gordan coefficients" are found in tables in many books, are merely the expansion coefficients

For an electron [in a "hydrogen-like" atom] having both orbital angular momentum and spin angular momentum, the eigenfunctions of $\mathbf{H}$, $\mathbf{S}^2$, $\mathbf{L}^2$, $\mathbf{J}^2$, $\mathbf{J}_z$ operators are the functions:

$$R_{nl}(r) \cdot |l, s; j, m_j\rangle$$

The eigenstates $l=1$ $s=\frac{1}{2}$ $j = l+s = 3/2$ $\overset{m_j}{\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}}$

and $j = l-s = 1/2$ $\frac{1}{2}, -\frac{1}{2}$

are called $\underset{\text{four states}}{{}^2P_{3/2}}$ and $\underset{\text{two states}}{{}^2P_{1/2}}$ (a "doublet" of states) but actually six states altogether.

$\boxed{{}^{(2s+1)}l_j}$ is called a TERM SYMBOL

SPIN-ORBIT COUPLING

The $|\ell\ s;\ j\ m_j\rangle$ states

Two-component function for the $^2P_{3/2}$ state:

$$\frac{1}{[2\ell+1]^{1/2}} R_{n\ell}(r) \begin{pmatrix} [\ell+1/2+m_j]^{1/2} Y_{\ell\, m_j-1/2}(\theta,\phi) \bullet \alpha \\ \\ -[\ell+1/2-m_j]^{1/2} Y_{\ell\, m_j+1/2}(\theta,\phi) \bullet \beta \end{pmatrix}$$

and the $^2P_{1/2}$ state:

$$\frac{1}{[2\ell+1]^{1/2}} R_{n\ell}(r) \begin{pmatrix} [\ell+1/2-m_j]^{1/2} Y_{\ell\, m_j-1/2}(\theta,\phi) \bullet \alpha \\ \\ [\ell+1/2+m_j]^{1/2} Y_{\ell\, m_j+1/2}(\theta,\phi) \bullet \beta \end{pmatrix}$$

Note that due to spin-orbit coupling, the good quantum numbers are ℓ s j m_j
not m_ℓ not m_s

Neglecting spin-orbit coupling:

$$\begin{pmatrix} R_{n\ell}(r) Y_{\ell\, m}(\theta,\phi) \bullet \alpha \\ \\ R_{n\ell}(r) Y_{\ell\, m}(\theta,\phi) \bullet \beta \end{pmatrix}$$

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
    - 5.1 The central field approximation and the Periodic Table
    - 5.2 Consequences of the Indistinguishability of Electrons and the Electron Spin
    - 5.3 Coupling of Angular Momenta
        - 5.3.1 Spin-Orbit Coupling
        - 5.3.2 How to Represent the Eigenfunctions for a System in which two Angular Momenta are Coupled?
    - **5.4 Electronic States of Atoms, Term Symbols, The Ground States of Atoms, Hund's Rules**
    - 5.5 Atomic Spectra of Light Atoms, e.g., Na

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
    - 5.1 The central field approximation and the Periodic Table
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        - 5.3.1 Spin-Orbit Coupling
        - 5.3.2 How to Represent the Eigenfunctions for a System in which two Angular Momenta are Coupled?
    - 5.4 Electronic States of Atoms, Term Symbols, The Ground States of Atoms, Hund's Rules
    - **5.5 Atomic Spectra of Light Atoms, e.g., Na**

Energy levels in a homogeneous magnetic field, the magnetic moment associated with angular mom.

Classical:

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$\vec{\mathcal{E}} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi$$

$\vec{A}(\vec{r},t)$ magnetic vector potential

$\Phi(\vec{r},t)$ scalar electromagnetic potential

$$\underset{\text{classical}}{\mathcal{H}} = \left(\frac{\vec{p} - \frac{q}{c}\vec{A}}{2m}\right)^2 + (V + q\phi)$$

potential of non-EM field

scalar

$$\underset{Q.M}{\mathcal{H}} = \left(\frac{\frac{\hbar}{i}\vec{\nabla} - \frac{q}{c}\vec{A}}{2m}\right)^2 + (V + q\phi)$$

$$= \frac{-\hbar^2}{2m}\nabla^2 + (V + q\phi)$$

$$- \frac{q\hbar}{2mci}(\vec{\nabla}\cdot\vec{A} + \vec{A}\cdot\vec{\nabla})$$

$$+ q^2 A^2 / 2mc^2$$

For a particle of charge q in a homog. magn. field $\vec{B}$ (along z dir.)

$$\phi = 0$$

$$\vec{A} = \frac{1}{2} \vec{B} \times \vec{r}$$

$$= -\frac{B_z y}{2} \hat{\imath} + \frac{B_z x}{2} \hat{\jmath}$$

$$\vec{B} = \vec{\nabla} \times \vec{A} = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ -\frac{B_z y}{2} & +\frac{B_z x}{2} & 0 \end{vmatrix} = B_z \hat{k}$$

ok

With this expression for $\vec{A}$:

$$\vec{\nabla} \cdot \vec{A} = -\frac{B_z}{2} \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right)$$

$$\vec{A} \cdot \vec{\nabla} = -\frac{B_z}{2} \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) = \frac{B_z}{2} \frac{i L_z}{\hbar}$$

$$A^2 = \left(-\frac{B_z}{2} y \right)^2 + \left(\frac{B_z x}{2} \right)^2 = \frac{B_z^2}{4} (x^2 + y^2)$$

$$-\frac{q\hbar}{2mci} \left(\vec{\nabla} \cdot \vec{A} + \vec{A} \cdot \vec{\nabla} \right) = -\frac{q}{2mc} B_z L_z$$

$$\mathcal{H} = \frac{-\hbar^2}{2m}\nabla^2 + V - \frac{q}{2mc} B_z L_z + \frac{q^2 B_z^2}{8mc^2}(x^2+y^2)$$

First order Zeeman effect B_z is not too large so that

$$\left\langle \underbrace{\frac{e^2 B_z^2}{8mc^2}(x^2+y^2)}_{\text{neglect this quadratic term}} \right\rangle << \left\langle \frac{eB_z}{2mc} l_z \right\rangle$$

for H atom:

$$\mathcal{H} = \frac{-\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{l^2}{2\mu r^2} + V(r) + \frac{e}{2\mu c} B_z l_z$$

because $[l^2, l_z] = 0$

then $[\mathcal{H}, L^2] = 0$, $[\mathcal{H}, l_z] = 0$ for this hamiltonian.

$\therefore$ $\mathcal{H}, l^2, l_z$ are still simult. knowable constants of the motion if we can neglect B_z^2 term

$\therefore$ $\psi_{nlm}(r) = R_{nl}(r)\, Y_{lm}(\theta\phi)$ still are good eigenfns satisfying

$\mathcal{H}\psi_{nlm} = E\psi_{nlm}$

$$\left\{-\frac{\hbar^2}{2\mu}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \boxed{\frac{l(l+1)\hbar^2}{2\mu r^2}} + V(r)\right\} R_{nl}(r)\, Y_{lm}(\theta,\phi)$$

$$+ \frac{eB_z}{2\mu c} m\hbar\, R_{nl}(r)\, Y_{lm}(\theta,\phi) = E\psi_{nlm} \quad = E_0 + \overbrace{\frac{eB_z}{2\mu c}\boxed{m\hbar}}^{-\mu\cdot B \text{ or } -\mu_z B_z}$$

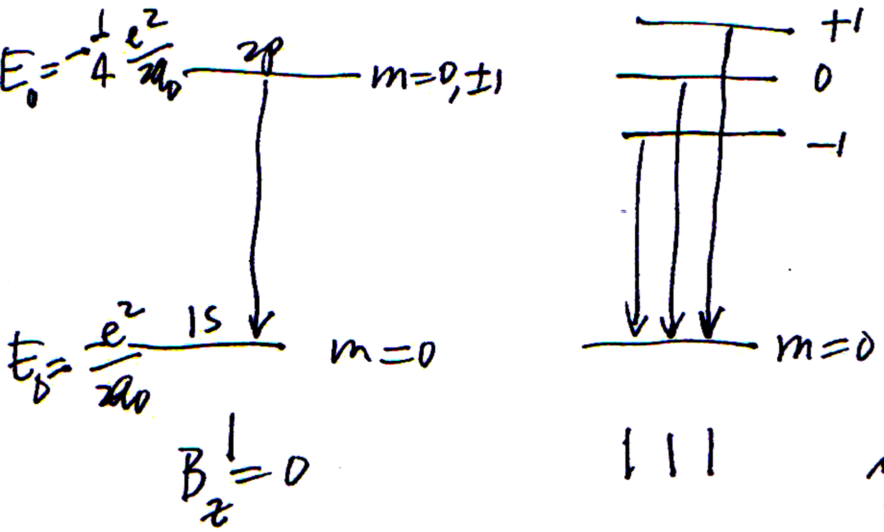
same radial eqn has to be solved

$$\frac{e\hbar}{2\mu c} = \mu_B$$

Bohr magneton

Thus it is as if there is a magnetic moment with a z component of magnitude $-m\mu_B$

$$E = E_0 + m\,\mu_B B_z$$

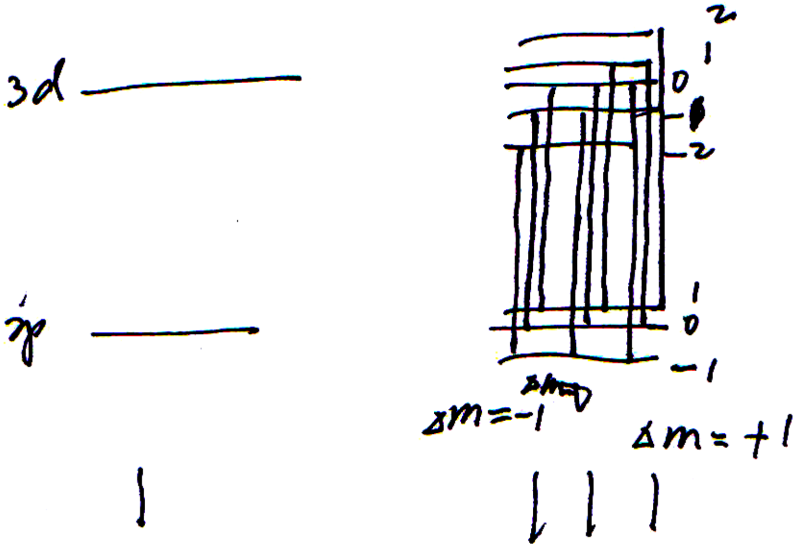


$-\frac{1}{4}\frac{e^2}{2a_0} + \mu_B B_z$

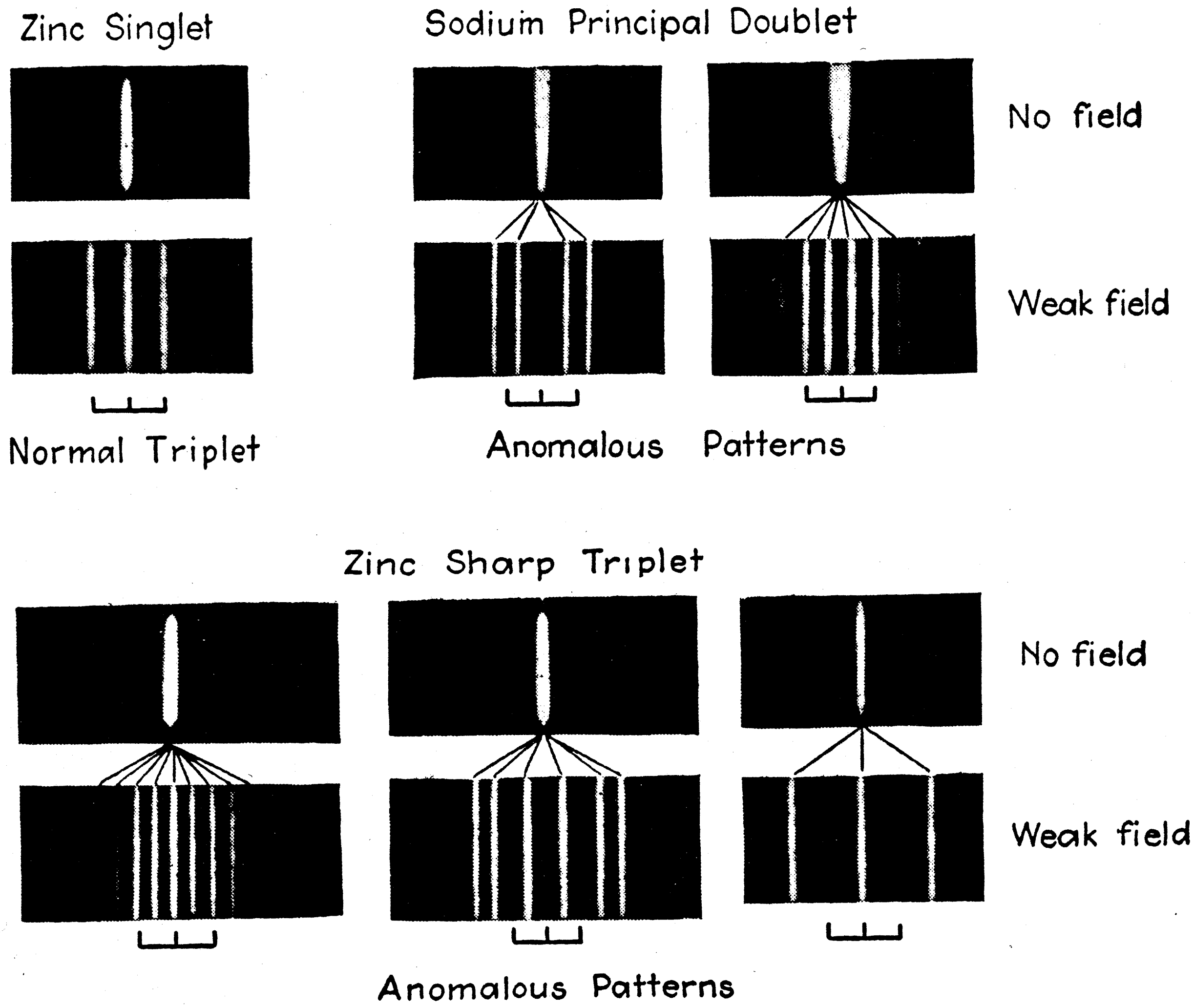
$-\frac{1}{4}\frac{e^2}{2a_0}$

$E = -\frac{1}{4}\frac{e^2}{2a_0} - \mu_B B_z$

spectrum splits into 3 lines



However anomalous Zeeman effect



Normal and anomalous Zeeman effect. Viewed perpendicular to the magnetic field.