October 17

October 21

Lectures #12 and #13

Second quantization

Evaluation of one and two-particle matrix elements

Coulomb matrix elements: example of two-particle operator (second quantization form)

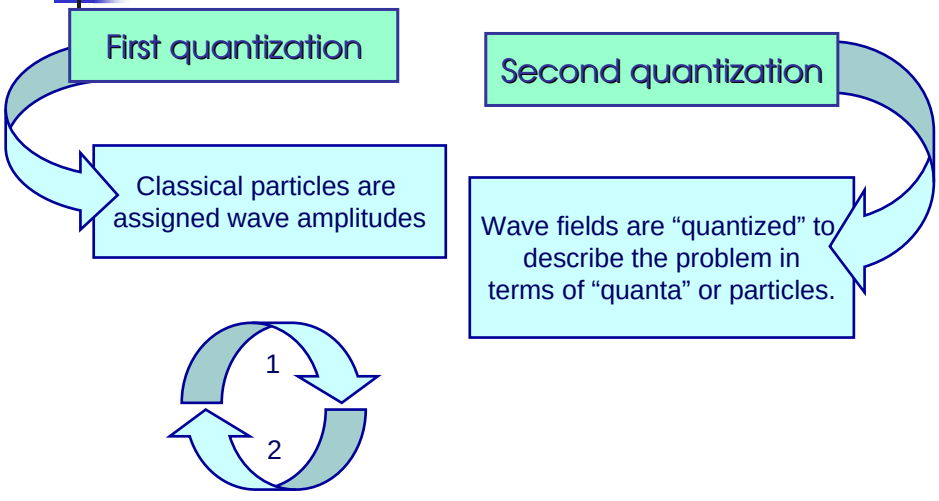
Helium atom: LS coupled states

Chapter 4, pages 95-99, 102-106, Lectures on Atomic Physics

Chapter 11, pages 241-246, Atomic many-body theory

I. Lindgren and J. Morrison

First & second quantization



Second quantization: atomic electrons (fermions)

One-electron state |k>
Described by the wave function $\Psi_k(\mathbf{r}_i)$

$$|k\rangle = a_k^\dagger |0\rangle$$

Creation operator

Vacuum state
(no electrons)

$$\langle 0|0\rangle = 1$$

Second quantization: atomic electrons (fermions)

One-electron state |k>
Described by the wave function $\Psi_k(q_i)$

Vacuum state
(no electrons)

$$\langle 0|0\rangle = 1$$

$$|k\rangle = a_k^\dagger |0\rangle$$ Creation operator

$$\langle k| = \langle 0| a_k$$ ← Annihilation operator

$a_k |0\rangle = 0$: "there are no electrons to annihilate in a vacuum"

$$\langle 0| a_k^\dagger = 0$$

Anticommutation relations

$$\left\{a_i^\dagger, a_j^\dagger\right\} = a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$$

$$\left\{a_i, a_j\right\} = a_i a_j + a_j a_i = 0$$

$$\left\{a_i, a_j^\dagger\right\} = a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}$$

$a_k|0\rangle = 0$

$\langle 0|a_k^\dagger = 0$

Orthonormality of one-electron states:

$$\langle i|j\rangle = \langle 0|a_i a_j^\dagger|0\rangle = \langle 0|\delta_{ij} - a_j^\dagger a_i|0\rangle = \delta_{ij}$$

Two-electron states

First quantizaiton: Slater determinant

Second quantizaiton

$$\Psi_{jk}(q_1,q_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_j(q_1) & \psi_k(q_2)\\ \psi_j(q_2) & \psi_k(q_2)\end{vmatrix} \Rightarrow |jk\rangle = a_j^\dagger a_k^\dagger|0\rangle$$

Orthonormality of two-electron states:

$$\langle\Psi_{ij}(q_1,q_2)|\Psi_{kl}(q_1,q_2)\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$$

$$\langle ij|kl\rangle = \langle 0|a_j a_i a_k^\dagger a_l^\dagger|0\rangle$$

NOTE: reversed order

Need to evaluate

Orthonormality of two-electron states

$$\langle ij|kl\rangle = \langle 0|a_j a_i a_k^\dagger a_l^\dagger|0\rangle = ?$$

Lets transform $a_j a_i a_k^\dagger a_l^\dagger$ to "normal form":

Move: Creation operators | Annihilation operators

left ← → right

Use anticommutation relations to move a_i to the right

$$a_j a_i a_k^\dagger a_l^\dagger = a_j a_l^\dagger \delta_{ik} - a_j a_k^\dagger a_i a_l^\dagger = \delta_{ik}\delta_{jl} - a_l^\dagger a_j \delta_{ik} - \delta_{jk} a_i a_l^\dagger + a_k^\dagger a_j a_i a_l^\dagger$$
$$= \delta_{ik}\delta_{jl} - a_l^\dagger a_j \delta_{ik} - \delta_{jk}\delta_{il} + \delta_{jk} a_l^\dagger a_i + a_k^\dagger a_j \delta_{il} - a_k^\dagger a_j a_l^\dagger a_i =$$
$$= \delta_{ik}\delta_{jl} - a_l^\dagger a_j \delta_{ik} - \delta_{jk}\delta_{il} + \delta_{jk} a_l^\dagger a_i + a_k^\dagger a_j \delta_{il} - \delta_{jl} a_k^\dagger a_i + a_k^\dagger a_l^\dagger a_j a_i$$

Orthonormality of two-electron states

$$\langle ij|kl\rangle = \langle 0|a_j a_i a_k^\dagger a_l^\dagger|0\rangle = ?$$

Lets transform $a_j a_i a_k^\dagger a_l^\dagger$ to "normal order":

Normal order with respect to vacuum → Creation operators | Annihilaiton operators

left ← → right

Use anticommutation relations to move a_i and a_j to the right

$$a_j a_i a_k^\dagger a_l^\dagger = a_j a_l^\dagger \delta_{ik} - a_j a_k^\dagger a_i a_l^\dagger = \delta_{ik}\delta_{jl} - a_l^\dagger a_j \delta_{ik} - \delta_{jk} a_i a_l^\dagger + a_k^\dagger a_j a_i a_l^\dagger$$
$$= \delta_{ik}\delta_{jl} - a_l^\dagger a_j \delta_{ik} - \delta_{jk}\delta_{il} + \delta_{jk} a_l^\dagger a_i + a_k^\dagger a_j \delta_{il} - a_k^\dagger a_j a_l^\dagger a_i =$$
$$= \delta_{ik}\delta_{jl} - a_l^\dagger a_j \delta_{ik} - \delta_{jk}\delta_{il} + \delta_{jk} a_l^\dagger a_i + a_k^\dagger a_j \delta_{il} - \delta_{jl} a_k^\dagger a_i + a_k^\dagger a_l^\dagger a_j a_i$$

$$\langle ij|kl\rangle = \langle 0|a_j a_i a_k^\dagger a_l^\dagger|0\rangle$$

Normal order of operators

Why do we want to transform to normal order?
To calculate expectation values: expectation value of normal ordered operators is zero.

$$a_j a_i a_k^\dagger a_l^\dagger = \delta_{ik}\delta_{jl} - a_l^\dagger a_j \delta_{ik} - \delta_{jk}\delta_{il} + \delta_{jk} a_l^\dagger a_i + a_k^\dagger a_j \delta_{il} - \delta_{jl} a_k^\dagger a_i + a_k^\dagger a_l^\dagger a_j a_i$$

$$\langle 0|a_j a_i a_k^\dagger a_l^\dagger|0\rangle = \delta_{ik}\delta_{jl} - \langle 0|a_l^\dagger a_j|0\rangle \delta_{ik} - \delta_{jk}\delta_{il} + \delta_{jk}\langle 0|a_l^\dagger a_i|0\rangle$$

$$+\langle 0|a_k^\dagger a_j|0\rangle \delta_{il} - \delta_{jl}\langle 0|a_k^\dagger a_i|0\rangle + \langle 0|a_k^\dagger a_l^\dagger a_j a_i|0\rangle$$

$$= \delta_{ik}\delta_{jl} - \delta_{jk}\delta_{il}$$

0 0 0 0 0

Exactly the result we had in first quantization

Many-particle operators in second quantization

$a_i^\dagger|0\rangle$ one-particle state

States

$a_i^\dagger a_j^\dagger|0\rangle$ two-particle state

$a_i^\dagger a_j^\dagger \ldots a_n^\dagger|0\rangle$ N-particle state

} described by Slater determinants in first quantization

Operators

First quantizaiton **Second quantizaiton**

One-particle operator $F = \sum_{i=1}^{N} f(\mathbf{r}_i) \longrightarrow F = \sum_{i,j} f_{ij}\, a_i^\dagger a_j$

Two-particle operator $G = \frac{1}{2}\sum_{i\neq j} g(r_{ij}) \longrightarrow G = \frac{1}{2}\sum_{i,j} g_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k$

$g_{ijkl} = g_{jilk}$

Many-particle operators in second quantization

First and second quantization description must produce identical results; however, is it more convenient to use second quantization for calculation of properties of many-electro systems as the antisymmetrization properties are carried by the operators rather than the wave functions as in the case of Slater determinants.

$$F = \sum_{i,j} f_{ij}\, a_i^\dagger a_j \qquad G = \frac{1}{2}\sum_{i,j} g_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k$$

$$f_{ab} = \langle a | f | b \rangle = \int d^3 r\, \psi_a^\dagger(\mathbf{r})\, f(\mathbf{r}) \psi_b(\mathbf{r})$$

$$g_{abcd} = \langle ab | g | cd \rangle = \int d^3 r_1 \int d^3 r_2\, \psi_a^\dagger(\mathbf{r}_1) \psi_b^\dagger(\mathbf{r}_2)\, g(\mathrm{r}_{12})\, \psi_c(\mathbf{r}_1) \psi_d(\mathbf{r}_2)$$

The rules for calculating matrix elements are equivalent, for example:

$$\langle ab | G | ab \rangle = \frac{1}{2}\sum_{ijkl} g_{ijkl} \langle 0 | a_b a_a a_i^\dagger a_j^\dagger a_l a_k a_a^\dagger a_b^\dagger | | 0 \rangle = g_{abab} - g_{abba}$$

Examples of one and two-particle operators

First quantizaiton | **Second quantizaiton**

1

$$H_0 = \sum_{i=1}^{N} h_i \qquad H_0 = \sum_{i=1}^{N} \varepsilon_i\, a_i^\dagger a_i$$

$h_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}$

eigenvalue of h_i

2

Coulomb ($1/r_{12}$) interaction: two-particle operator

$$H' = \frac{1}{r_{12}} \qquad H' = \frac{1}{2}\sum_{ijkl} g_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k$$

two-electron matrix element of the Coulomb potential $1/r_{12}$

$$g_{abcd} = \int d^3 r_1 \int d^3 r_2\, \psi_a^\dagger(\mathbf{r}_1) \psi_b^\dagger(\mathbf{r}_2) \frac{1}{\mathrm{r}_{12}} \psi_c(\mathbf{r}_1) \psi_d(\mathbf{r}_2)$$

He-like systems revisited

$H_0 = \sum_{i=1}^{N} \varepsilon_i \, a_i^\dagger a_i$

Two-electron state $|ab\rangle = a_a^\dagger a_b^\dagger |0\rangle$ is an eigenfunction of H_0 with an eigenvalue $E_{ab}^{(0)} = \varepsilon_a + \varepsilon_b$:

$$H_0 |ab\rangle = (\varepsilon_a + \varepsilon_b) |ab\rangle$$

However, it is not necessarily an angular momentum eigenstate.

Lets construct eigenstates of $\{H, \mathbf{L}^2, L_z, \mathbf{S}^2, S_z\}$ from $|ab\rangle$ states.

$\mathbf{L} = \boldsymbol{l}_a + \boldsymbol{l}_b$

$\mathbf{S} = \boldsymbol{s}_a + \boldsymbol{s}_b$

First, we couple l_a and l_b to construct eigenstates of $\mathbf{L}^2$, L_z with eigenvalues L(L+1) and M_L

S=0: singlet state
S=1: triplet states

Second, we couple s_a and s_b to construct eigenstates of $\mathbf{S}^2$, S_z with eigenvalues S(S+1) and M_S

$s_a = s_b = 1/2 \longrightarrow$ S=0,1

He-like systems: construction of coupled states

$$|ab\rangle = a_a^\dagger a_b^\dagger |0\rangle$$

Therefore, the coupled states are given by the sum over magnetic moments which contains two Clebsch-Gordon coefficients:

$$|ab, LM_L, SM_S\rangle = \eta \sum_{m_a m_b} \sum_{\mu_a \mu_b} - \underset{l_b m_b}{\overset{l_a m_a}{}} - \underset{\tfrac{1}{2}\,\mu_b}{\overset{\tfrac{1}{2}\,\mu_a}{}} \; a_a^\dagger a_b^\dagger |0\rangle$$

(LM_L, SM_S)

Normalization factor

$$\langle ab, LM_L, SM_S | ab, LM_L, SM_S \rangle = \eta^2 \left(1 + (-1)^{L+S} \delta_{n_a n_b} \delta_{l_a l_b}\right)$$

$$\eta = \begin{cases} 1 & n_a \neq n_b, l_a \neq l_b \\ \dfrac{1}{\sqrt{2}} & \text{Identical orbitals } n_a = n_b, l_a = l_b \end{cases}$$

He-like systems: First-order energy

$$\left|ab, LM_L, SM_S\right\rangle = \eta \sum_{m_a m_b} \sum_{\mu_a \mu_b} - \underset{l_b m_b}{\overset{l_a m_a}{\overset{\downarrow}{\overset{\downarrow}{}}}} \; LM_L \; - \underset{\tfrac{1}{2}\,\mu_b}{\overset{\tfrac{1}{2}\,\mu_a}{\overset{\downarrow}{\overset{\downarrow}{}}}} \; SM_S \quad a_a^\dagger a_b^\dagger \left|0\right\rangle$$

The first-order energy is given by

$$E^{(1)} = \left\langle ab, LM_L, SM_S \right| H' \left| ab, LM_L, SM_S \right\rangle$$

$$H' = \frac{1}{2} \sum_{ijkl} g_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k$$

$$g_{abcd} = \int d^3 r_1 \int d^3 r_2\, \psi_a^\dagger(\mathbf{r}_1) \psi_b^\dagger(\mathbf{r}_2) \frac{1}{r_{12}} \psi_c(\mathbf{r}_1) \psi_d(\mathbf{r}_2)$$

Coulomb matrix element

First, lets consider Coulomb matrix element

$$g_{abcd} = \int d^3 r_1 \int d^3 r_2\, \psi_a^\dagger(\mathbf{r}_1) \psi_b^\dagger(\mathbf{r}_2) \frac{1}{r_{12}} \psi_c(\mathbf{r}_1) \psi_d(\mathbf{r}_2)$$

The functions ψ are given by $\psi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \phi)$

The $1/r_{12}$ can be expanded as

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} Y_{kq}^*(\theta_1, \phi_1) Y_{kq}(\theta_2, \phi_2)$$

This expression may be re-written using C-tensors defined by

$$C_q^k(\hat{r}) = \sqrt{\frac{4\pi}{(2k+1)}} Y_{kq}(\theta, \phi)$$

$$\frac{1}{r_{12}} = \frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} (-1)^q\, C_q^k(\hat{r}_1)\, C_{-q}^k(\hat{r}_2)$$

Coulomb matrix element

We now substitute the expressions for ψ and $1/r_{12}$ back into our matrix element and separate dr and dΩ integrals

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} (-1)^q \, C_q^k(\hat{r}_1) \, C_{-q}^k(\hat{r}_2)$$

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta,\phi)$$

$$g_{abcd} = \int d^3r_1 \int d^3r_2 \, \psi_a^\dagger(\mathbf{r}_1)\psi_b^\dagger(\mathbf{r}_2) \frac{1}{r_{12}} \psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2)$$

$R_k(abcd)$ — radial integral

$$= \sum_{k=0}^{\infty} \left[\int_0^\infty dr_1 \, r_1^2 \int_0^\infty dr_2 \, r_2^2 R_{n_a l_a}(r_1) R_{n_b l_b}(r_2) \frac{r_<^k}{r_>^{k+1}} R_{n_c l_c}(r_1) R_{n_d l_d}(r_2) \right]$$

$$\times \sum_{q=-k}^{k} (-1)^q \left[\int d\Omega_1 Y_{l_a m_a}(\theta_1,\phi_1) \, C_q^k(\theta_1,\phi_1) Y_{l_c m_c}(\theta_1,\phi_1) \right] \rightarrow \langle l_a m_a | C_q^k | l_c m_c \rangle$$

$$\left[\int d\Omega_2 Y_{l_b m_b}(\theta_2,\phi_2) \, C_{-q}^k(\theta_2,\phi_2) Y_{l_d m_d}(\theta_2,\phi_2) \right] \rightarrow \langle l_b m_b | C_{-q}^k | l_d m_d \rangle$$

Coulomb matrix element

$$g_{abcd} = \sum_{k=0}^{\infty} R_k(abcd) \sum_{q=-k}^{k} (-1)^q \langle l_a m_a | C_q^k | l_c m_c \rangle \langle l_b m_b | C_{-q}^k | l_d m_d \rangle$$

Next, we use Wigner-Eckart theorem for both of the matrix elements:

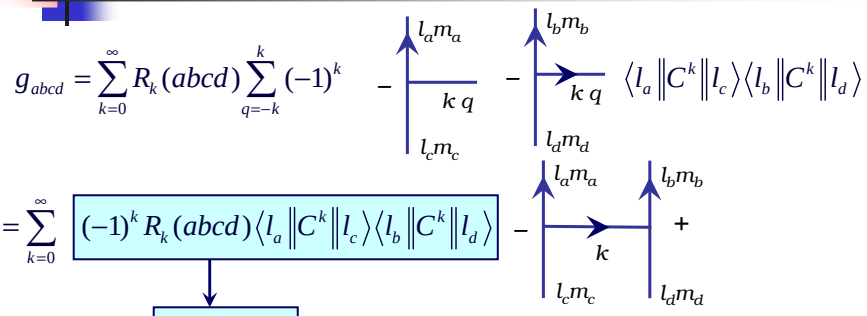
$$g_{abcd} = \sum_{k=0}^{\infty} R_k(abcd) \sum_{q=-k}^{k} (-1)^q \; - \begin{array}{c} l_a m_a \\ \uparrow \\ \hline k \; q \\ l_c m_c \end{array} \; - \begin{array}{c} l_b m_b \\ \uparrow \\ \hline k \; -q \\ l_d m_d \end{array} \; \langle l_a \| C^k \| l_c \rangle \langle l_b \| C^k \| l_d \rangle$$

We use $- \begin{array}{c} l_b m_b \\ \uparrow \\ \hline k \; -q \\ l_d m_d \end{array} = (-1)^{k-q} - \begin{array}{c} l_b m_b \\ \uparrow \\ \hline k \; q \\ l_d m_d \end{array}$

Note: k and q are integers

Coulomb matrix element

$$g_{abcd} = \sum_{k=0}^{\infty} R_k(abcd) \sum_{q=-k}^{k} (-1)^k$$

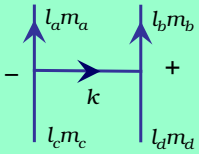


$$\langle l_a \| C^k \| l_c \rangle \langle l_b \| C^k \| l_d \rangle$$

$$= \sum_{k=0}^{\infty} (-1)^k R_k(abcd) \langle l_a \| C^k \| l_c \rangle \langle l_b \| C^k \| l_d \rangle$$

$$X_k(abcd)$$

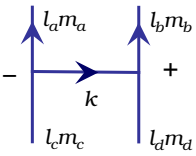
$$g_{abcd} = \sum_{k=0}^{\infty}$$



$$X_k(abcd)$$

Summary: Coulomb matrix element (non-relativistic case)

$$g_{abcd} = \sum_{k=0}^{\infty}$$



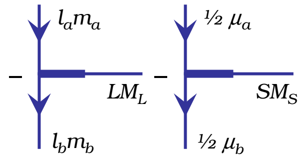
$$X_k(abcd)$$

$$X_k(abcd) = (-1)^k R_k(abcd) \langle l_a \| C^k \| l_c \rangle \langle l_b \| C^k \| l_d \rangle$$

$$R_k(abcd) = \int_0^{\infty} dr_1\, r_1^2 \int_0^{\infty} dr_2\, r_2^2 R_{n_a l_a}(r_1) R_{n_b l_b}(r_2) \frac{r_<^k}{r_>^{k+1}} R_{n_c l_c}(r_1) R_{n_d l_d}(r_2)$$

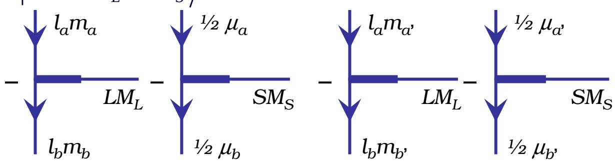
$$\langle l_1 \| C^k \| l_2 \rangle = (-1)^{l_1} \sqrt{(2l_1+1)(2l_2+1)} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix}$$

Back to He-like systems

$$\left|ab, LM_L, SM_S\right\rangle = \eta \sum_{m_a m_b} \sum_{\mu_a \mu_b}$$  $$a_a^\dagger a_b^\dagger \left|0\right\rangle$$

Assume
$l_a = l_{a'}$
$l_b = l_{b'}$

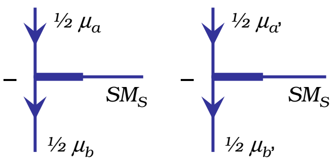
$$E^{(1)} = \left\langle ab, LM_L, SM_S \right| H' \left| ab, LM_L, SM_S \right\rangle$$

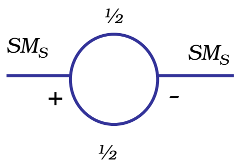
$$= \eta^2 \sum_{m_a m_b} \sum_{\mu_a \mu_b} \sum_{m_{a'} m_{b'}} \sum_{\mu_{a'} \mu_{b'}}$$ 

$$\times \left(g_{a'b'ab}\, \delta_{\mu_a \mu_{a'}} \delta_{\mu_b \mu_{b'}} - g_{a'b'ba}\, \delta_{\mu_a \mu_{b'}} \delta_{\mu_b \mu_{a'}} \right)$$

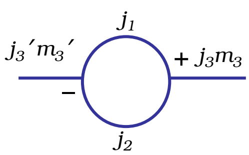
$$H' = \frac{1}{2} \sum_{ijkl} g_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k ; \quad \left\langle ab \right| G \left| ab \right\rangle = g_{abab} - g_{abba}$$

Sum over μ's: Term 1

$$Term\,1: \quad \sum_{\mu_a \mu_b} \sum_{\mu_{a'} \mu_{b'}} \delta_{\mu_a \mu_{a'}} \delta_{\mu_b \mu_{b'}}$$ 

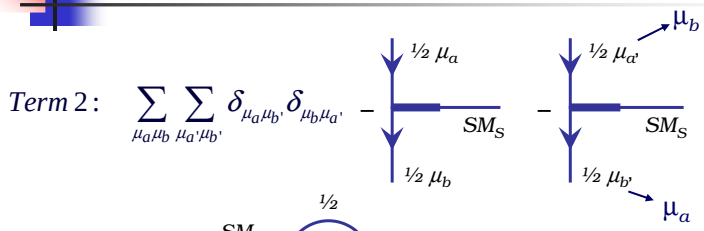
$$= (2S+1)$$  $$= 1$$

We used orthogonality relation to evaluate this diagram

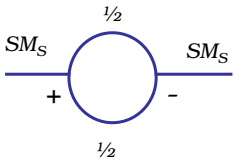
 $$= \frac{1}{2j_3+1} \delta_{j_3' j_3} \delta_{m_3' m_3}$$

Sum over μ's: Term 2

$$Term\,2: \sum_{\mu_a\mu_b}\sum_{\mu_{a'}\mu_{b'}} \delta_{\mu_a\mu_{b'}}\delta_{\mu_b\mu_{a'}}$$



$$= (2S+1)(-1)^{S+1}$$

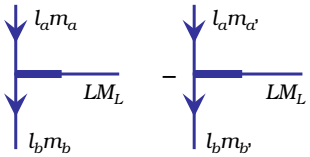


$$= -(-1)^{S}$$

Extra phase factor

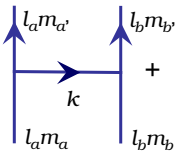
First-order energy: He-like systems

$$E^{(1)} = \eta^2 \sum_{m_{a'}m_{b'}} \sum_{m_a m_b} \sum_{k}$$

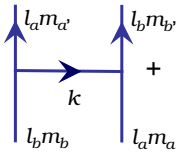


Assume
$l_a = l_{a'}$
$l_b = l_{b'}$

$$\times\Big($$



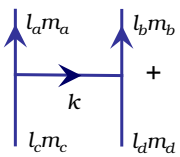
$$X_k(abab) + (-1)^S$$



$$X_k(abba)\Big)$$

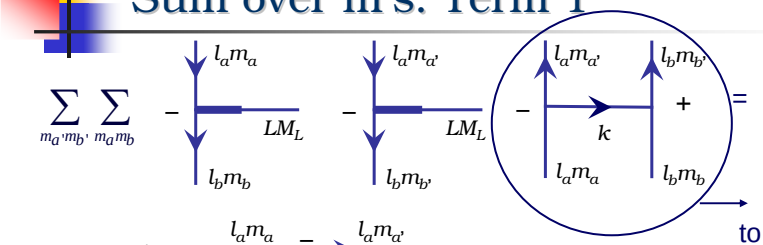
where we substituted Coulomb matrix elements g into our formula

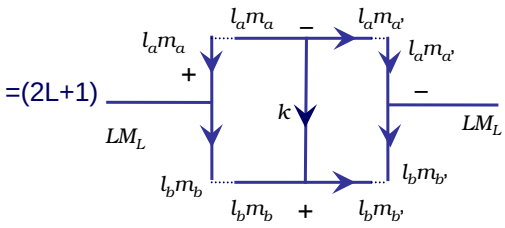
$$g_{abcd} = \sum_{k=0}^{\infty}$$



$$X_k(abcd)$$

Sum over m's: Term 1



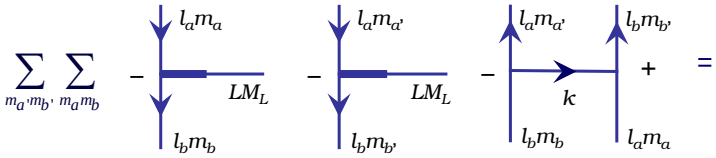


1) Remove triangle (get 6-j symbol)

2) Use orthogonality relation
(get factor 1/(2L+1)

$$= (-1)^{L+k+l_a+l_b} \begin{Bmatrix} l_a & l_b & L \\ l_b & l_a & k \end{Bmatrix}$$

Sum over m's: Term 2



$$= (-1)^{k+l_a+l_b} \begin{Bmatrix} l_a & l_b & L \\ l_a & l_b & k \end{Bmatrix}$$

The calculation is very similar to Term1, only need to switch a and b lines in the first angular diagram.

$|ab, LM_L, SM_S\rangle$

Final expression:
First order energy for He-like system

$$E^{(1)} = \eta^2 \sum_k \left\{ (-1)^{L+k+l_a+l_b} \begin{Bmatrix} l_a & l_b & L \\ l_b & l_a & k \end{Bmatrix} X_k(abab) + (-1)^{S+k+l_a+l_b} \begin{Bmatrix} l_a & l_b & L \\ l_a & l_b & k \end{Bmatrix} X_k(abba) \right\}$$

$$X_k(abcd) = (-1)^k R_k(abcd) \langle l_a \| C^k \| l_c \rangle \langle l_b \| C^k \| l_d \rangle$$

$$R_k(abcd) = \int_0^\infty dr_1\, r_1^2 \int_0^\infty dr_2\, r_2^2 R_{n_a l_a}(r_1) R_{n_b l_b}(r_2) \frac{r_<^k}{r_>^{k+1}} R_{n_c l_c}(r_1) R_{n_d l_d}(r_2)$$

$$\langle l_1 \| C^k \| l_2 \rangle = (-1)^{l_1} \sqrt{(2l_1+1)(2l_2+1)} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{Bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{Bmatrix} = 1$$

Special case: if $l_a = l_b = 0$ *(s states)* $\rightarrow \langle s \| C^k \| s \rangle = \delta_{k0}$