e^2/r_{ij} and Slater Sum Rule Method

LAST TIME:

1. $\mathbf{L}^2,\mathbf{S}^2$ method for setting up $|NLM_LSM_S\rangle$ many-electron basis states in terms of linear combination of Slater determinants
   * $M_L = 0$, $M_S = 0$ block: $\mathbf{L}^2 \rightarrow \mathbf{L}_+\mathbf{L}_-$
     $\mathbf{S}^2 \rightarrow \mathbf{S}_+\mathbf{S}_-$
   * diagonalize $\mathbf{S}^2$ (singlets and triplets)
   * diagonalize $\mathbf{L}^2$ in same basis that diagonalizes $\mathbf{S}^2$
   [Recall: to get matrix elements of $\mathbf{L}^2$, first evaluate $\mathbf{L}^2\left|\left|\left|\psi_i\right|\right|\right\rangle$ and then left multiply by $\left\langle\left|\left|\psi_j\right|\right|\right|$
2. coupled representations $|nj\omega\ell s\rangle$ and $|NJLSM_J\rangle$
3. Projection operators: automatic projection of $\mathbf{L}^2$ eigenfunctions* remove unwanted L ″ part
   * preserve normalization of wanted L′ part
   * remove overlap factor

TODAY:

1. Slater Sum Rule Trick (trace invariance): MAIN IDEA OF LECTURE.
2. evaluate $\sum_{i>j} e^2/r_{ij}$ matrix elements (tedious, but good for you)

   [2-e^- operator, spatial coordinates only, scalar wrt **J,L,S**]

   * *multipole expansion* of charge distribution due to "other electrons"
   * matrix element selection rules for e^2/r_{ij} in both Slater determinantal and many-e^- basis sets
   * Gaunt Coefficients (c^k) (tabulated) and Slater-Condon (F^k,G^k) Coulomb and Exchange parameters. Because of sum rule, can evaluate mostly $\left\langle ab\left|\frac{1}{r_{ij}}\right|ab\right\rangle$ and $\left\langle ab\left|\frac{1}{r_{ij}}\right|ba\right\rangle$ type matrix elements and never $\left\langle ab\left|\frac{1}{r_{ij}}\right|cd\right\rangle$ type matrix elements.
3. Apply Sum Rule Method
4. Hund's 1st and 2nd Rules

1. Slater's Sum Rule Method

It is almost always possible to evaluate e^2/r_{ij} matrix elements without solving for all $|LM_LSM_S\rangle$ basis states.

* trace of any Hermitian matrix, expressed in ANY representation, is the sum of the eigenvalues of that matrix (thus invariant to unitary transformation)

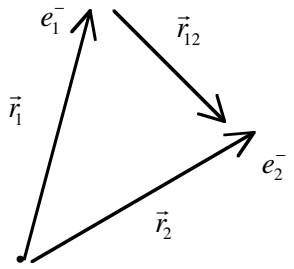
* $\sum_{i>j} e^2 / r_{ij}$ and every scalar operator with respect to $\hat{\mathbf{J}}$ (or $\hat{\mathbf{L}}$,$\hat{\mathbf{S}}$) has nonzero matrix elements *diagonal* in J *and* M_J (or L and M_L) and *independent* of M_J or (M_L,M_S)

[W-E Theorem: **J** is a GENERIC ANGULAR MOMENTUM with respect to which e^2/r_{ij} is classified]

Recall from definition of r_{12}, that e^2/r_{ij} is a scalar operator with respect to $\hat{\mathbf{J}}$, $\hat{\mathbf{L}}$, $\hat{\mathbf{S}}$ but not with respect to $\mathbf{j}_i$ or $\boldsymbol{\ell}_i$.

Interelectronic Repulsion: $\sum_{i>j} e^2/r_{ij}$

* destroys orbital approximation ∅ $$ for electronic structure calculations
* "correlation energy," "shielding"



$$e_1^- \text{ at } (r_1, \theta_1, \phi_1)$$

$$e_2^- \text{ at } (r_2, \theta_2, \phi_2)$$

scalar with respect to **J**, **L**, **S**, $\mathbf{s}_i$ but not $\mathbf{j}_i$, $\boldsymbol{\ell}_i$ ⟶

$$\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$$

$$r_{12}^2 = r_1^2 - 2r_1 \cdot r_2 + r_2^2$$

$$r_{12} = \left[r_1^2 + r_2^2 - 2|r_1||r_2|\cos(\vec{r}_1, \vec{r}_2) \right]^{1/2}$$

expand r_{12}^{-1} as power series in $\left(\frac{r_<}{r_>}\right)$

where $r_<$ is smaller of $|r_1|,|r_2|$

(integrals evaluated in 2 regions : $r_1 < r_2,\ r_2 < r_1$)

lengthy algebra [see Eyring, Walter, and Kimball "Quantum Chemistry" pages 369-371 and, for relationship between Legendre polynomials and $Y_\ell^m(\theta,\phi)$, pages 52-59.]

multipole expansion

$$\frac{1}{r_{ij}} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left(\frac{4\pi}{2n+1}\right) \frac{r_<^n}{r_>^{n+1}} Y_n^m(\theta_i,\phi_i)\left[Y_n^m(\theta_j,\phi_j)\right]^*$$

2^n-pole moment (n=0 monopole, n=1 dipole,…)

not principal q.n.!

convergent series

angular momenta magnitude n, projection m

scalar product of 2 angular momenta, one for i-th particle, one for j-th

* converts m to –m

n-pole charge distribution ∅ n-th rank tensor ∅ 2n+1 components

No dependence on s, so $1/r_{ij}$ is scalar with respect to **S**, $\mathbf{s}_i$, $\mathbf{s}_j$.

$\left[Y_n^m(\theta_i,\phi_i) = \langle \theta_i,\phi_i \,|\, \ell_i = n, m_{\ell_i} = m \rangle\right]$

The reason for this rather complicated looking expansion is that it is well suited for integrals over atomic orbitals which are expressed in terms of r_i, θ_i, ϕ_i, which are coordinates of the i-th e^- with respect to the center of symmetry (nucleus) rather than the other e^-. It enables use of AO basis states. Otherwise $1/r_{ij}$ integrals would be nightmares.

Selection rules for matrix elements:

$$\text{orbitals}\begin{cases} |\Delta\ell_i| \le n \;,\; \Delta m_{\ell_i} = m \;,\; \Delta m_{s_i} = 0 \\ |\Delta\ell_j| \le n \;,\; \Delta m_{\ell_j} = -m \;,\; \Delta m_{s_j} = 0 \end{cases}$$

not principal q. n.

term in multipole expansion

triangle rule, $|\ell_i - \ell'_i| \le n \le \ell_i + \ell'_i$

(steps of 2 because of parity)

overall: $\Delta L = 0$, $\Delta S = 0$, $\Delta M_L = 0$, $\Delta M_S = 0$, and indep. of M_L, M_S

Can use any M_L, M_S from box diagram.

It is also clear how to evaluate the angular factors of the atomic orbital matrix elements using 3-j coefficients. Special tables of "Gaunt Coefficients" (also C&S pages 178-179, Golding, page 41, see handout).

general $1/r_{12}$ matrix element ($\Delta so = 0$, 1, and 2 are possible)

$$\overset{e_2^{\pm}}{\overbrace{\langle\|ab\|\|1/r_{12}\|\|cd\|\rangle}}\underset{e_1^{\pm}}{} = \left\langle \|ab\| \left| \frac{1}{r_{12}} \right| \|cd\| \right\rangle - \left\langle \|ab\| \left| \frac{1}{r_{12}} \right| \|dc\| \right\rangle$$

$$\left\langle ab \left| \frac{1}{r_{12}} \right| cd \right\rangle = \underbrace{\delta(m_{s_a}, m_{s_c})\delta(m_{s_b}, m_{s_d})}_{\text{** } 1/r_{12} \text{ does not operate on spin coodinates **}} \underbrace{\delta(m_{\ell_a} + m_{\ell_b}, m_{\ell_c} + m_{\ell_d})}_{\substack{1/r_{12} \text{ scalar with respect to } \hat{L}_{12} = \hat{\ell}_1 + \hat{\ell}_2}} \times$$

$$\underbrace{\sum_{k=0}^{\infty}}_{\substack{\text{tensor rank for product of AOs occupied by } e^{\pm} \#1 \text{ must be same as for } \#2 \text{ for scalar product of n-th rank tensors}}} \underbrace{c^k(\ell_a m_{\ell_a}, \ell_c m_{\ell_c})}_{e_1^-} \underbrace{c^k(\ell_b m_{\ell_b}, \ell_d m_{\ell_d})}_{e_2^-} \times$$

GAUNT COEFFICIENTS — ANGULAR FACTOR OF INTEGRAL

$$\underbrace{R^k(n_a \ell_a n_b \ell_b n_c \ell_c n_d \ell_d)}_{\text{radial factor}}$$

$$\underbrace{c^k(\ell m_\ell, \ell' m_{\ell'})}_{\text{tabulated}} \equiv \left[\frac{2\ell'+1}{2\ell+1}\right]^{1/2} \underbrace{A^{k\ell\ell'}_{000} A^{k\ell'\ell}_{m_\ell - m'_\ell, m'_\ell, -m_\ell}}_{\substack{\text{Clebsch-Gordan coefficients that result from integral over product of 3 spherical harmonics — one from operator, two from orbitals}}}$$

triangle rule: $|\ell - \ell'| \le k \le \ell + \ell'$

$\ell + \ell' + k = \text{even}$ $\left(\text{from properties of } A^{k\ell\ell'}_{000}\right)$ (parity)

restrictions on k and m:

$$\left\langle n_1 \ell_1 m_{\ell_1} \left| Y_k^m \right| n_1' \ell_1' m_{\ell_1}' \right\rangle$$

e_1^- integral; $m_{\ell_1}' + m = m_{\ell_1}$; triangle rule

for intraconfiguration matrix elements, $R^k(abcd)$ takes on especially simple form (because the same one or two orbitals appear in the bra and in the ket).

$$\left.\begin{aligned} R^k(ab,ab) &\equiv F^k(a,b) \\ R^k(ab,ba) &\equiv G^k(a,b) \end{aligned}\right\} \text{“Slater – Condon” parameters}$$

(these are reduced matrix elements dependent only on ℓ_a, ℓ_b, ℓ_c, ℓ_d and not on any of the m_ℓ quantum numbers.) All L-S states from one configuration are expressed in terms of the same set of F^k, G^k parameters.

$$\left\langle \|ab\| \left| \frac{e^2}{r_{12}} \right| \|ab\| \right\rangle = \mathbf{J}(a,b) - \delta\left(m_{s_a}, m_{s_b}\right)\mathbf{K}(a,b)$$

DIRECT; EXCHANGE; spins must match or K term vanishes

$$\mathbf{J}(a,b) \equiv \left\langle ab \left| \frac{e^2}{r_{12}} \right| ab \right\rangle = \sum_{k=0}^{\infty} \underbrace{c^k\left(\ell_a m_{\ell_a}, \ell_a m_{\ell_a}\right) c^k\left(\ell_b m_{\ell_b}, \ell_b m_{\ell_b}\right)}_{a^k\left(\ell_a m_{\ell_a}, \ell_b m_{\ell_b}\right)} \times F^k\left(n_a \ell_a, n_b, \ell_b\right)$$

$$\left[\iint a^*(1)a(1)\hat{O}pb^*(2)b(2)d\tau_1 d\tau_2\right]$$

charge distributions

$$\mathbf{K}(a,b) \equiv \left\langle ab \left| \frac{e^2}{r_{12}} \right| ba \right\rangle = \delta\left(m_{s_a}, m_{s_b}\right) \sum_{k=0}^{\infty} \underbrace{\left[c^k\left(\ell_a m_{\ell_a}, \ell_b m_{\ell_b}\right)\right]^2}_{b^k\left(\ell_a m_{\ell_a}, \ell_b m_{\ell_b}\right)} G^k\left(n_a \ell_a, n_b \ell_b\right)$$

$$\left[\iint a^*(1)b(1)\hat{O}pa(2)b^*(2)d\tau_1 d\tau_2\right]$$

something else!

for special cases, such as nd^2, $n_a\ell_a = n_b\ell_b$ and $F^k = G^k$

Now we are ready to use tables of c^k (or, more conveniently, a^k and b^k) to set up e^2/r_{ij} matrix

Easy example: nf^2 (recall ^1I, ^3H, ^1G, ^3F, ^1D, ^3P, ^1S)

$$\left.\begin{aligned} \left|{}^1I\ 60\right\rangle &= \left\|3\alpha 3\beta\right\| \\ \left|{}^3H\ 51\right\rangle &= \left\|3\alpha 2\alpha\right\| \end{aligned}\right\}$$

these are the only L-S states represented by a single Slater determinant — extremes of M_L,M_S box diagram

since e^2/r_{ij} is a scalar operator with respect to $\hat{\mathbf{L}}$, $\hat{\mathbf{S}}$, $\hat{\mathbf{J}}$, matrix elements are M_L, M_S, M_J independent — so we can use *any* M_L,M_S component to evaluate the matrix element — whichever is most convenient!

$$\left\langle {}^1I\left|\frac{e^2}{r_{12}}\right|{}^1I\right\rangle = \sum_{k=0,2,4,6} c^k(\underbrace{33}_{\ell m_\ell},33)c^k(33,33)F^k(nf,nf) - \underbrace{\delta(\alpha,\beta)}_{\substack{=0 \\ \text{one spin } \alpha \\ \text{other spin } \beta}}\sum_k \left[c^k(33,33)\right]^2 G^k(nf,nf)$$

(2ℓ under the first sum; $F^k(nf^2)$ under G^k)

$$= \sum_{k=0,2,4,6} \left[c^k(33,33)\right]^2 F^k(nf,nf)$$

$$\left\langle {}^3H\left|\frac{e^2}{r_{12}}\right|{}^3H\right\rangle = \sum_{k=0,2,4,6} \left\{\left[c^k(33,33)c^k(32,32)\right]F^k(nf,nf) - \underbrace{\left[c^k(33,32)\right]^2}_{\text{both spins } \alpha} G^k(nf,nf)\right\}$$

(e_1^- under the first c^k; e_2^- under the second c^k; $F^k(nf^2)$ under G^k)

(a,a) (b,b) (a,b)

Here is where everyone makes mistakes!

Use table of c^k in Golding/C&S handout (C&S page 179).

Note that $[1/7361 \cdot 64]^{1/2}$ is implicit after the first entry for f^2, $k = 6$.

	k = 0	2	4	6
$c^k(33,33)$	1	–1/3	1/11	$-[1/7361\bullet 64]^{1/2}$
$c^k(32,32)$	1	0	–7/33	$-[6/7361\bullet 64]^{1/2}$
$c^k(33,32)$	0	+1/3	$-30^{1/2}/33$	$-[7/7361\bullet 64]^{1/2}$
D_k	1	225	$1089 = 33^2$	$7361\bullet 64$

convenient factor

D_k is a factor that simplifies the expressions. Each term has the form F^k/D_k. Call this ratio F_k. Get simpler looking expressions when you replace F^k by D_kF_k (D_k appears in denominators of c^k as $[\ldots/D_k]^{1/2}$)

$$\left\langle {}^1I\left|\frac{e^2}{r_{12}}\right|{}^1I\right\rangle = F^0 + \left(\frac{1}{9}\right)F^2 + \left(\frac{1}{121}\right)F^4 + \left(\frac{1}{7361\cdot 64}\right)F^6$$

$$= F_0 + 25F_2 + 9F_4 + F_6$$

Always have two factors of c^k. Thus F^k gets divided by D_k to yield F_k.

$$\left\langle {}^3H\left|\frac{e^2}{r_{12}}\right|{}^3H\right\rangle = F^0 + \left[\left(-\frac{1}{3}\right)(0) - (1/3)^2\right]F^2 + \left[\left(\frac{1}{11}\right)\left(\frac{-7}{33}\right) - \frac{30}{33\cdot 33}\right]F^4 + \left[\frac{-6-7}{7361\cdot 64}\right]F^6$$

$$= F^0 - \frac{1}{9}F^2 - \frac{51}{(33)^2}F^4 \frac{-13}{7361\cdot 64}F^6$$

$$= F_0 - 25F_2 - 51F_4 - 13F_6$$

A lot of book – keeping, but easy to learn how to use tables of c^k, a^k, b^k, D_k.

But it is much more work for f^3 than for f^2.

SUM RULE METHOD:

Basic idea is that the sum of diagonal elements in the single Slater determinant basis set within an M_L, M_S box is equal to the sum of the eigenvalues!

Look at $M_L = 3, M_S = 1$ box: $\|3\alpha 0\alpha\|$ and $\|2\alpha 1\alpha\|$. This box generates $|{}^3H\ 31\rangle$ and $|{}^3F\ 31\rangle$, but trace is $E({}^3H) + E({}^3F)$ and we already know $E({}^3H)$!

So $E({}^1I) = \langle\|3\alpha 3\beta\|\rangle$

$$E({}^3H) = \langle\|3\alpha 2\alpha\|\rangle$$

$$E({}^3F) = \langle\|3\alpha 0\alpha\|\rangle + \langle\|2\alpha 1\alpha\|\rangle - E({}^3H)$$

$$E({}^1G) = \langle\|3\alpha 1\beta\|\rangle + \langle\|3\beta 1\alpha\|\rangle + \langle\|2\alpha 2\beta\|\rangle - E({}^1I) - E({}^3H)$$

$$E({}^1D) = \langle\|3\alpha - 1\beta\|\rangle + \langle\|3\beta - 1\alpha\|\rangle + \langle\|2\alpha 0\beta\|\rangle + \langle\|2\beta 0\alpha\|\rangle$$

$$+\langle\|1\alpha 1\beta\|\rangle - E({}^1I) - E({}^1G) - E({}^3H) - E({}^3F)$$

$$E({}^3P) = \langle\|3\alpha - 2\alpha\|\rangle + \langle\|2\alpha - 1\alpha\|\rangle + \langle\|1\alpha 0\alpha\|\rangle - E({}^3H) - E({}^3F)$$

$$E({}^1S) = \text{sum of seven } \langle\|\ \|\rangle \ - \ \text{sum of six } E({}^{2S+1}L)$$

This seems rather laborious, but it is much easier than:

* generating each $|\, LM_L = L \;\; SM_S = S\rangle$ as an explicit linear combination of Slater determinants
* then calculating matrix elements of e^2/r_{ij}, because there are many nonzero off-diagonal matrix elements between Slater determinants in the same M_L,M_S box.

Here is the final result for the energies of all $(nf)^{2\ 2S+1}L$ terms:

$$E = E^{(0)} + E^{(1)} + E^{(2)}$$

$$E^{(0)} = \text{ sum of orbital energies from } h^{(0)} = -\frac{Z^2\Re}{n^2} = \varepsilon_{n\ell}$$

Bare nucleus hydrogenic orbital energy — or partly shielded by filled shells.

$$E^{(1)} = \underbrace{\left\langle e^2/r_{ij} \right\rangle}_{\text{ready now}} + \underbrace{\langle \mathbf{H}^{SO} \rangle}_{\text{next lecture}}$$

$$E^{(2)} = \left(\text{intra}\underline{\text{}}\text{configurational spin-orbit}\right) + \left(\text{inter}\underline{\text{}}\text{configurational } e^2/r_{ij}\right)$$

CI

For nf^2

shielded by all filled subshells

shielded by same subshell

^{1}I	$2\varepsilon_{nf}$	$+ F_0(nf^2)$	$+ 25\,F_2(nf^2)$	$+ 9\,F_4(nf^2)$	$+ F_6(nf^2)$
^{3}H	$2\varepsilon_{nf}$	$+ F_0$	$- 25\,F_2$	$- 51\,F_4$	$- 13\,F_6$
^{1}G	$2\varepsilon_{nf}$	$+ F_0$	$- 30\,F_2$	$+ 97\,F_4$	$+ 78\,F_6$
^{3}F	$2\varepsilon_{nf}$	$+ F_0$	$- 10\,F_2$	$- 33\,F_4$	$- 286\,F_6$
^{1}D	$2\varepsilon_{nf}$	$+ F_0$	$+ 19\,F_2$	$- 99\,F_4$	$+ 715\,F_6$
^{3}P	$2\varepsilon_{nf}$	$+ F_0$	$+ 45\,F_2$	$+ 33\,F_4$	$- 1287\,F_6$
^{1}S	$2\varepsilon_{nf}$	$+ F_0$	$+ 60\,F_2$	$+ 198\,F_4$	$+ 1716\,F_6$

shielded-core configurational energy

intraconfiguration L-S term splittings

(there is NO center of Gravity Rule for degeneracy weighted L-S terms)

Now it is easy to show that all F_k's are > 0 and $F_k >> F_{k+2}$ etc. (roughly factor of 10 per step in k)

From this we get an **empirical rule**

Lowest E of all L–S terms is the one with

* MAXIMUM S
* of those with Maximum S, lowest is the one with MAXIMUM L

These are Hund's **first** and **second** (of three) rules.

Note also that Hund's rules do nothing about predicting the energy order of L-S terms except for the identity of the single, lowest energy L-S term.

Nonlecture

There are several interesting problems also solved by this e^2/r_{ij} formalism.

1. Energy splittings between and Slater determinantal characters of two or more L,S terms of the same L and S that belong to the same L,S configuration

   e.g. $d^3 \rightarrow$ two ^{2}D terms

   see pages 47 - 50 of Golding for 2×2 secular determinant for ^{2}D of d^3

2. matrix elements of e^2/r_{ij} between same–L,S terms that belong to two different configurations

   e.g. nd^2 $^1S, ^3P, ^1D, ^3F, ^1G$

   $ndn'd$ $\left\{ \begin{matrix} ^1S, ^3P, ^1D, ^3F, ^1G \\ ^3S, ^1P, ^3D, ^1F, ^3G \end{matrix} \right\}$ no Pauli restrictions

   so there will be $^1S \sim ^1S$

   $^3P \sim ^3P$

   $^1D \sim ^1D$

   $^3F \sim ^3F$

   $^1G \sim ^1G$

   interconfigurational CI's, and each of these 5 interaction matrix elements will NOT be of the same magnitude.