**5.73 Lecture #34**

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

**LAST TIME:**
1. The $L^2, S^2$ matrix method for setting up $|NLM_sM_m\rangle$ many-electron basis states in terms of linear combination of Slater determinants
   \[ L^2 \rightarrow L_+L_- \]
   * $M_L = 0, M_s = 0$ block: $S^2 \rightarrow S_+S_-$

   * diagonalize $S^2$ (singlets and triplets)
   * diagonalize $L^2$ in same basis that diagonalizes $S^2$
   [Recall: to get matrix elements of $L^2$, first evaluate $L^2 \langle \psi_i \| \psi_j \rangle$ and then left multiply by $\langle \psi_j \| \psi_i \rangle$]
2. coupled representations $|nj\ell\omega\rangle$ and $|NJLSM\rangle$
3. Projection operators: automated projection of $L^2$ eigenfunctions
   * remove unwanted $L''$ part
   * preserve normalization of wanted $L'$ part
   * remove overlap factor
   * easy to write computer program that automates the projection method

**TODAY:**
1. Slater Sum Rule Trick (based on trace invariance): MAIN IDEA OF LECTURE.
2. Evaluate $\sum_{i>j} e^2/r_{ij}$ matrix elements (tedious, but good for you)
   \[ 1/r_{ij} \text{ is a } 2 - e^- \text{ operator that involves spatial coordinates only, scalar with respect to } J, L, \text{ and } S. \]
   * 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 the sum rule, can evaluate most $\langle ab | 1/r_{ij} | ab \rangle$
   and $\langle ab | 1/r_{ij} | ba \rangle$ type matrix elements and never need to evaluate $\langle ab | 1/r_{ij} | cd \rangle$-type matrix elements except when the configuration includes two same-$L,S$ terms.
3. Apply Sum Rule Method
4. Hund’s 1st and 2nd Rules

*updated August 28, 2020 @ 11:19 AM*
1. **Slater's Sum Rule Method**

It is almost always possible to evaluate $e^2/r_{ij}$ matrix elements without solving for all $|LM_lS_Ms\rangle$ 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 $\mathbf{J}$ (or $\mathbf{L}, \mathbf{S}$) has non-zero 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: $\mathbf{J}$ is the 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 $\mathbf{J}, \mathbf{L}, \mathbf{S}$ but not with respect to $\mathbf{j}_i$, or $\mathbf{\ell}_i$.

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

- destroys the single-electron orbital approximation $|n\ell\lambda\rangle$ for electronic structure calculations
- "correlation energy," "shielding" $\square$

![Diagram](image-url)

$e^-_1$ at $(r_1, \theta_1, \phi_1)$

$e^-_2$ at $(r_2, \theta_2, \phi_2)$

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

\[
\mathbf{r}_{12}^2 = \mathbf{r}_1^2 - 2\mathbf{r}_1 \cdot \mathbf{r}_2 + \mathbf{r}_2^2
\]

\[
\mathbf{r}_{12} = \left[ \mathbf{r}_1^2 + \mathbf{r}_2^2 - 2 \mathbf{r}_1 \mathbf{r}_2 \cos(\mathbf{r}_1, \mathbf{r}_2) \right]^{1/2}
\]
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expand $r_{i2}^{-1}$ as power series in $\left(\frac{r_1}{r_2}\right)$

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

(integrals evaluated in 2 regions: $r_1 < r_2, r_2 < r_1$) the larger $r_i$ is seeing the multipoles of the smaller $r_j$

...lengthy algebra...

will evaluate for orbitals occupied by $i$th e-

\[
\frac{1}{r_{ij}} = \sum_{\ell=0}^{\infty} \sum_{m=-n}^{n} \left(\frac{4\pi}{2n+1}\right) \frac{r_{i}^{\ell}}{r_{i}^{n+1}} Y_{n}^{m}(\theta_{i}, \phi_{i}) Y_{n}^{m}(\theta_{j}, \phi_{j})
\]

An n-pole charge distribution is an n-th rank tensor with 2n+1 components.

No dependence on electron spin, so $1/r_{ij}$ is scalar with respect to $S, s_i, s_j$.

\[
Y_{n}^{m}(\theta_{i}, \phi_{i}) = \left[ \begin{array}{c} \theta_{i} \phi_{i} \\ \ell_{i} = n, m_{\ell_{i}} = m \end{array} \right]
\]
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 \( r_i, \theta_i, \phi_i \), which are the coordinates of the \( i \)-th \( e^- \) with respect to the center of symmetry (nucleus) rather than the other \( e^- \). It enables use of atomic orbital basis states. Otherwise the \( 1/r_{ij} \) integrals would be nightmares.

\[
Y^m_n(\theta, \phi) = \langle \theta, \phi \mid n = \ell, m = m_i \rangle
\]

**Selection rules** for matrix elements:

\[
\langle \ell_i m_i \mid Y^m_n \mid \ell_i' m_i' \rangle \langle \ell_j m_j \mid Y^m_n \mid \ell_j' m_j' \rangle
\]

orbits

\[
\begin{cases}
|\Delta \ell_i| \leq n, & \Delta m_{\ell_i} = m, \quad \Delta m_{s_i} = 0 \\
|\Delta \ell_j| \leq n, & \Delta m_{\ell_j} = -m, \quad \Delta m_{s_j} = 0
\end{cases}
\]

triangle rule, \( |\ell_i - \ell_j| \leq n \leq \ell_i + \ell_j \)

(term in multipole expansion)

(non-zero for steps in \( n \) of an even number because of parity)

\[
! \begin{cases}
\Delta L = 0, \Delta S = 0, \Delta M_L = 0, \Delta M_S = 0, \text{ and independent of } M_L, M_S. \text{ Can use any } M_L, M_S \text{ Slater determinant from the box diagram.}
\end{cases}
\]

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 Condon and Shortley pages 178-179, Golding, page 41).
general $1/r_{12}$ matrix element (non-zero matrix elements of the $1/r_{12}$ operator follow the $\Delta s-o = 0, 1, \text{and } 2$ spin-orbital selection rule for change in spin-orbitals)

$$\left\langle e_{1}^{+} \left\| \frac{1}{r_{12}} \right\| e_{2}^{-} \right\rangle = \left\langle ab \left\| \frac{1}{r_{12}} \right\| cd \right\rangle - \left\langle ab \left\| \frac{1}{r_{12}} \right\| dc \right\rangle$$

$$\left\langle ab \left\| \frac{1}{r_{12}} \right\| cd \right\rangle = \delta(m_{s_{a}}, m_{s_{b}})\delta(m_{s_{c}}, m_{s_{d}})\delta(m_{\ell_{a}} + m_{\ell_{b}}, m_{\ell_{c}} + m_{\ell_{d}}) \times 1/r_{12} \text{ scalar with respect to } L_{12} = \hat{\ell}_{1} + \hat{\ell}_{2} \text{ (can't change } M_{\ell})$$

$$\sum_{k=0}^{\infty} \frac{c^{k}(\ell_{a} m_{\ell_{a}}, \ell_{c} m_{\ell_{c}}) c^{k}(\ell_{b} m_{\ell_{b}}, \ell_{d} m_{\ell_{d}}) R^{k}(n_{a} \ell_{a} n_{b} \ell_{b} n_{c} \ell_{c} n_{d} \ell_{d})}{e_{1}^{e_{1}} e_{2}^{e_{2}}}$$

tensor rank for product of AOs occupied by $e^{-}$ #1 must be same as for $e^{-}$ #2 for scalar product of two n-th rank tensors

$$c^{k}(\ell m_{\ell}, \ell' m_{\ell'}) \equiv \left[ \frac{2\ell' + 1}{2\ell + 1} \right]^{1/2}$$

tabulated

$$A_{000}^{k \ell \ell'} A_{m_{\ell}-m_{\ell'},m'_{\ell}-m_{\ell}}^{k \ell' \ell}$$

Clebsch-Gordan coefficients that result from integral over the product of three spherical harmonics — one from operator, two from orbitals

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

$\ell + \ell' + k = \text{ even } (\text{from properties of } A_{000}^{k \ell \ell'} ) (\text{including parity})$
For intra-configuration matrix elements, $R^k(abcd)$ has an especially simple form (because the same one or two orbitals appear in both the bra and in the ket).

\[
R^k(ab,ab) \equiv F^k(a,b)
\]  

\[
R^k(ab,ba) \equiv G^k(a,b)
\]  

(These are reduced matrix elements dependent only on $\ell_a$, $\ell_b$, $\ell_c$, $\ell_d$ and not on any of the $m$ quantum numbers.) All $L$-$S$ states that belong to the same configuration are expressed in terms of the same set of $F^k$, $G^k$ parameters.

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

(spins must match or $K$ term will vanish)  

(Direct Exchange)  

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

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

for special cases, such as $nd^2$, we have the simplified result that $n_a \ell_a = n_b \ell_b$ and $F^k = G^k$

Now we are ready to set up tables of $c^k$ (or, more conveniently, $a^k$ and $b^k$) to evaluate the $e^2/r_{ij}$ matrix.
Easy example: nf^2  

(recall that L-S terms of f^2 are \(^1I, ^3H, ^1G, ^3F, ^1D, ^3P, ^1S\))

\[ \begin{align*}
1I \ 60 & = \| 3\alpha 3\beta \| \\
3H \ 51 & = \| 3\alpha 2\alpha \|
\end{align*} \]  

\(^1I\) and \(^3H\) are the only L-S states from the \(f^2\) configuration that are represented by a single Slater determinant — extremes of the \(M_L,M_S\) box diagram.

[You really do not want to calculate off-diagonal matrix elements of a two-electron operator if you can help it!]

Since \(e^2/r_{ij}\) is a scalar operator with respect to \(\hat{L}, \hat{S}, \hat{J}\), 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!

\[
\left\langle \begin{array}{c} 1I \\ \epsilon_{1}^{-} \end{array} \right| e^2 \left| \begin{array}{c} 1I \\ \epsilon_{1}^{-} \end{array} \right\rangle = \sum_{k=0,2,4,6} \left[ c^{k}(33,33)c^{k}(33,33)F^{k}(nf,nf) - \delta(\alpha,\beta) \sum_{k} \left[ c^{k}(33,33) \right]^{2} G^{k}(nf,nf) \right]_{F^{k}(nf^2)}
\]

\[
\left\langle \begin{array}{c} 3H \\ \epsilon_{1}^{-} \end{array} \right| e^2 \left| \begin{array}{c} 3H \\ \epsilon_{1}^{-} \end{array} \right\rangle = \sum_{k=0,2,4,6} \left\{ \left[ c^{k}(33,33)c^{k}(32,32) \right] F^{k}(nf,nf) - \left[ c^{k}(33,32) \right]^{2} G^{k}(nf,nf) \right\}_{F^{k}(nf^2)}
\]

Use table of \(c^k\) in Golding (page 41)/C&S handout (C&S page 179).

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

Here is where everyone makes mistakes!

<table>
<thead>
<tr>
<th>(k)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c^k(33,33))</td>
<td>1</td>
<td>-1/3</td>
<td>1/11</td>
<td>-[1/7361\cdot64]^{1/2}</td>
</tr>
<tr>
<td>(c^k(32,32))</td>
<td>1</td>
<td>0</td>
<td>-7/33</td>
<td>+[36/7361\cdot64]^{1/2}</td>
</tr>
<tr>
<td>(c^k(33,32))</td>
<td>0</td>
<td>+1/3</td>
<td>-30^{1/2}/33</td>
<td>+[7/7361\cdot64]^{1/2}</td>
</tr>
<tr>
<td>(D_k)</td>
<td>1</td>
<td>225</td>
<td>1089 = 33^2</td>
<td>7361\cdot64</td>
</tr>
</tbody>
</table>

C&S Table: the number listed goes inside the SQRT replacing the numerator in the first row.
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\( D_k \) is a factor that simplifies the expressions. Each term has the form \( F_k/D_k \). Call this ratio \( F_k \) [notice \( F_k \) vs. \( F_k \)]. Get simpler looking expressions when you replace \( F_k \) by \( D_kF_k \) \((D_k \) appears in denominators of \( c_k \) as \([.../D_k]^{1/2} \)

\[
\begin{align*}
\left\langle \begin{matrix} 1 \\ r_{12} \end{matrix} \right| e^2 \left| \begin{matrix} 1 \\ r_{12} \end{matrix} \right\rangle &= F^0 + \left( \frac{1}{9} \right) F^2 + \left( \frac{1}{121} \right) F^4 + \left( \frac{1}{7361 \times 64} \right) F^6 \\
&= F_0 + 25F_2 + 9F_4 + F_6
\end{align*}
\]

\[
\begin{align*}
\left\langle \begin{matrix} 3 \\ H \\ r_{12} \end{matrix} \right| e^2 \left| \begin{matrix} 3 \\ H \\ r_{12} \end{matrix} \right\rangle &= F^0 + \left[ \left( -\frac{1}{3} \right)(0) - \left( \frac{1}{3} \right)^2 \right] F^2 + \left[ \left( \frac{1}{11} \right) \left( -\frac{7}{33} \right) \right] F^4 + \left[ -\frac{6}{33} \right] F^6 \\
&= F^0 - \frac{1}{9} F^2 - \frac{51}{(33)^2} F^4 - \frac{13}{7361 \times 64} F^6
\end{align*}
\]

\[
\begin{align*}
&= F_0 - 25F_2 - 51F_4 - 13F_6
\end{align*}
\]

A lot of bookkeeping, but it's possible to learn how to use tables of \( c_k, a^k, b^k, \) and \( D_k \), except it is much more work for \( f_3 \) than for \( f_2 \) (but the job is not yet complete for the \( L-S \) terms beyond \(^1I\) and \(^3H\)!

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**SUM RULE METHOD:**

Basic idea is that the sum of all the 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 the \( M_L = 3, M_S = 1 \) box: \( |3\alpha0\alpha| \) and \( |2\alpha1\alpha| \). This box generates \( |3H31\rangle \) and \( |3F31\rangle \), but the trace is \( E(3H) + E(3F) \) and we already know \( E(3H) \)!

So

\[
\begin{align*}
E(\ ^1I) &= \langle |3\alpha3\beta| \rangle \\
E(\ ^3H) &= \langle |3\alpha2\alpha| \rangle \\
E(\ ^3F) &= \langle |3\alpha0\alpha| \rangle + \langle |2\alpha1\alpha| \rangle - E(\ ^3H) \\
E(\ ^1G) &= \langle |3\alpha1\beta| \rangle + \langle |3\beta1\alpha| \rangle + \langle |2\alpha2\beta| \rangle - E(\ ^1I) - E(\ ^3H) \\
E(\ ^1D) &= \langle |3\alpha - 1\beta| \rangle + \langle |3\beta - 1\alpha| \rangle + \langle |2\alpha0\beta| \rangle + \langle |2\beta0\alpha| \rangle \\
&\quad + \langle |1\alpha1\beta| \rangle - E(\ ^1I) - E(\ ^1G) - E(\ ^3H) - E(\ ^3F) \\
E(\ ^3P) &= \langle |3\alpha - 2\alpha| \rangle + \langle |2\alpha - 1\alpha| \rangle + \langle |1\alpha0\alpha| \rangle - E(\ ^3H) - E(\ ^3F) \\
E(\ ^1S) &= \text{sum of seven } \langle |\ | \rangle \text{ } - \text{sum of six } E(\ ^{2S+1}L)
\end{align*}
\]
This seems exceptionally laborious, but it is much easier than:

* generating each \( |LM_L = L \quad SM_S = S \rangle \) eigen-state 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 of the \((nf)^{2S+1}L\) terms:

\[ E = E^{(0)} + E^{(1)} + E^{(2)} \]

\[ E^{(0)} = \text{sum of orbital energies from } h^{(0)} = -\frac{Z^2 R}{n^2} = \varepsilon_{nf} \]

\[ E^{(1)} = \frac{1}{r_{ij}} \left( e^2 + H^{(SO)} \right) \]

\[ E^{(2)} = \left( \text{intraconfiguraional spin-orbit} \right) + \left( \text{interconfiguraional } e^2/r_{ij} \right) \]

For \( nf^2 \)

\[ 1^1I \quad 2\varepsilon_{nf} + F_0(nf^2) + 25F_2(nf^2) + 9F_4(nf^2) + F_6(nf^2) \]

\[ 3^3H \quad 2\varepsilon_{nf} + F_0 - 25F_2 - 51F_4 - 13F_6 \]

\[ 1^1G \quad 2\varepsilon_{nf} + F_0 - 30F_2 + 97F_4 + 78F_6 \]

\[ 3^3F \quad 2\varepsilon_{nf} + F_0 - 10F_2 - 33F_4 - 286F_6 \]

\[ 1^1D \quad 2\varepsilon_{nf} + F_0 + 19F_2 - 99F_4 + 715F_6 \]

\[ 3^3P \quad 2\varepsilon_{nf} + F_0 + 45F_2 + 33F_4 - 1287F_6 \]

\[ 1^1S \quad 2\varepsilon_{nf} + F_0 + 60F_2 + 198F_4 + 1716F_6 \]

(there is \textbf{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 $F_k \gg F_{k+2}$ etc. (by roughly a factor of 10 per step in $k$).

From this we get an empirical rule (empirical because we expect that contributions to $E(L, S)$ from $F_4$ and $F_6$ can be ignored).

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 make no predictions about the energy order of $L$-$S$ terms except for the identity of the single, lowest energy $L$-$S$ term.
Non-Lecture

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

1. The energy splittings between and the Slater determinantal characters of two or more $L_S$ terms of the same $L$ and $S$ that belong to the same electronic configuration

   \[ \text{e.g. } d^3 \rightarrow \text{two } ^2D \text{ terms} \]

   see pages 47-50 of Golding for $2 \times 2$ secular determinant for $^2D$ of $d^3$

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

   \[ \text{e.g. } nd^2 \quad ^1S,^3P,^1D,^3F,^1G \]

   ndn’d \[ \begin{cases} ^1S,^3P,^1D,^3F,^1G \\ ^3S,^1P,^3D,^1F,^3G \end{cases} \]

   no Pauli restrictions

So, for $L_S$ terms that belong to the nd2 configurations, there will be

\[ ^1S \sim ^1S \]
\[ ^3P \sim ^3P \]
\[ ^1D \sim ^1D \]
\[ ^3F \sim ^3F \]
\[ ^1G \sim ^1G \]

interconfigurational interaction matrix elements and each of these 5 interaction matrix elements will NOT be of the same magnitude. There will be different Configuration Interaction energy shifts for the various $L_S$ terms in a configuration.

Knowing the single configuration expected pattern of $L_S$ states (energies and other properties) enables detection of local inter-configuration perturbations. Predicted patterns are EVERYTHING to an experimentalist!