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

LAST TIME:

1. The $\mathbf{L}^2$,$\mathbf{S}^2$ matrix method for setting up $|NLM_LSM_S\rangle$ many-electron basis states in terms of linear combination of Slater determinants $\mathbf{L}^2 \rightarrow \mathbf{L}_+\mathbf{L}_-$
   * $M_L = 0$, $M_S = 0$ block: $\mathbf{S}^2 \rightarrow \mathbf{S}_+\mathbf{S}_-$

   * 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 $\mathbf{L}^2\, |\|\psi_i\|\rangle$ and then left multiply by $\langle\|\psi_j\||$]
2. coupled representations $|nj\omega\ell s\rangle$ and $|NJLSM_J\rangle$
3. Projection operators: automated projection of $\mathbf{L}^2$ eigenfunctions
   * remove unwanted L'' part
   * preserve normalization of wanted L' part
   * remove overlap factor
   * easy to write computer program that automates the projection method

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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)
   [$1/r_{ij}$ is a $2-e^-$ operator that involves spatial coordinates only, scalar with respect to **J, L,** 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 $\langle ab\left|\frac{1}{r_{ij}}\right|ab\rangle$ and $\langle ab\left|\frac{1}{r_{ij}}\right|ba\rangle$ type matrix elements and never need to evaluate $\langle ab\left|\frac{1}{r_{ij}}\right|cd\rangle$-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

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)

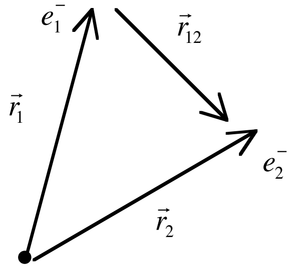
* $\sum_{i>j} e^2/r_{ij}$ and every scalar operator with respect to $\hat{J}$ (or $\hat{L},\hat{S}$) has non-zero matrix elements *diagonal* in J and M_J (or L and M_L) and *independent* of M_J (or M_L,M_S)

[W-E Theorem: **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 $\hat{\boldsymbol{J}},\hat{\boldsymbol{L}},\hat{\boldsymbol{S}}$ but not with respect to $\mathbf{j}_i$ or $\boldsymbol{\ell}_i$.

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"□



$$e_1^- \text{ at } (r_1,\theta_1,\phi_1)$$
$$e_2^- \text{ at } (r_2,\theta_2,\phi_2)$$

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

Scalar with respect to **J**, **L**, **S**, $\mathbf{s}_i$ but not $\mathbf{j}_i$, ℓ_i. Do you know why?

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

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

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

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 [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.]

will evaluate for orbitals occupied by i^th e^–

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

multipole expansion

$$\frac{1}{r_{ij}}=\sum_{\underset{\text{not principal q.n.!}}{\boxed{n}}=0}^{\infty}\ \sum_{m=-n}^{n}\left(\frac{4\pi}{2n+1}\right)\underbrace{\frac{r_<^{n}}{r_>^{n+1}}}_{\text{convergent series}}\ \underbrace{\underbrace{Y_n^m(\theta_i,\phi_i)\left[Y_n^m\right.}_{\text{angular momenta magnitude n, projection m}}\left.(\theta_j,\phi_j)\right]^{\circledast}}_{\text{scalar product of 2 angular momenta, one for i-th particle, one for j-th}}$$

$$\frac{1}{r_>}\left(\frac{r_<}{r_>}\right)^n$$

* converts m to –m

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.

$$\left[Y_n^m(\theta_i,\phi_i)=\left\langle\theta_i,\phi_i\middle|\ell_i=\underbrace{n,m_{\ell_i}=m}_{\text{indices of }Y_n^m}\right\rangle\right]$$

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 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 $1/r_\mathrm{ij}$ integrals would be nightmares.

$$Y_n^m(\theta,\phi) = \langle \theta,\phi | n = \ell, m = m_\ell \rangle$$

Selection rules for matrix elements:

$$\langle \ell_i m_i | Y_n^m | \ell_i' m_i' \rangle \langle \ell_j m_j | Y_n^m | \ell_j' m_j' \rangle$$

$\boxed{\text{not principal q. n.}}$

$$\text{orbitals}\underbrace{\begin{cases} |\Delta \ell_i| \le \textcircled{n}, & \Delta m_{\ell_i} = m, \quad \Delta m_{s_i} = 0 \\ |\Delta \ell_j| \le \textcircled{n}, & \Delta m_{\ell_j} = -m, \quad \Delta m_{s_j} = 0 \end{cases}}_{\text{triangle rule, } |\ell_i - \ell_i'| \le n \le \ell_i + \ell_i'}$$

$\boxed{\text{term in multipole expansion}}$

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

! overall: $\Delta L = 0$, $\Delta S = 0$, $\Delta M_L = 0$, $\Delta M_S = 0$, and independent of M_L, M_S. Can use any M_L, M_S Slater determinant from the 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 Condon and Shortley pages 178-179, Golding, page 41).

<u>general $1/r_{12}$ matrix element</u> (non-zero matrix elements of the $1/r_{12}$ operator follow the Δs-o = 0, 1, and 2 spin-orbital selection rule for change in spin-orbitals)

$$\left\langle \left\| \underbrace{a\overbrace{b \left\| 1/r_{12} \right\| c}^{e_2^-}}_{e_1^-} d \right\| \right\rangle = \left\langle ab\left|\frac{1}{r_{12}}\right|cd\right\rangle - \left\langle ab\left|\frac{1}{r_{12}}\right|dc\right\rangle$$

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

$$\underbrace{\sum_{k=0}^{\infty}}\ \underbrace{\underbrace{c^k\left(\ell_a m_{\ell a},\ell_c m_{\ell c}\right)}_{e_1^-}\underbrace{c^k\left(\ell_b m_{\ell b},\ell_d m_{\ell d}\right)}_{e_2^-}}_{\text{GAUNT COEFFICIENTS — ANGULAR FACTOR OF INTEGRAL}}\times \underbrace{R^k\left(n_a\ell_a n_b\ell_b n_c\ell_c n_d\ell_d\right)}$$

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

radial factor A “reduced matrix element” because all m quantum numbers are gone.

$$\underbrace{c^k\left(\ell m_\ell,\ell' m_{\ell'}\right)}_{\text{tabulated}} \equiv \left[\frac{2\ell'+1}{2\ell+1}\right]^{1/2} \underbrace{A_{000}^{k\ell\ell'}\,A_{m_\ell-m'_\ell,m'_\ell-m_\ell}^{k\ell'\ell}}$$

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

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

$\ell+\ell'+k =$ even $\quad$ (from properties of $A_{000}^{k\ell\ell'}$) (including parity) restrictions on k and m: e_1^- integral $m_{\ell_1}+m=m'_{\ell_1}$

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

triangle rule

For <u>intra</u>-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).

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

(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 that belong to the same configuration are expressed in terms of the same set of F^k, G^k parameters.

spins must match or K term will vanish

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

(This is how singlet and triplet states have different E even though $1/r_{ij}$ does not operate on the spin factor.)

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

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

classical charge distributions

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

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

something not *classical!*

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 ${}^1I$, ${}^3H$, ${}^1G$, ${}^3F$, ${}^1D$, ${}^3P$, ${}^1S$)

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

${}^1I$ 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 $\hat{\mathbf{L}}$, $\hat{\mathbf{S}}$, $\hat{\mathbf{J}}$, matrix elements are M_L, M_S, and M_J independent — so we can use *any* M_L,M_S component to evaluate the matrix element — whichever is most convenient!

$$\left\langle {}^1I\left|\frac{e^2}{r_{12}}\right|{}^1I\right\rangle = \sum_{k=0,2,4,\underset{\llcorner\,2\ell}{6}} c^k(\overset{\boxed{e_1^-}}{\underbrace{3\,3}_{\ell m_\ell},33})\,c^k(\overset{\boxed{e_2^-}}{33,33})F^k(nf,nf) - \underbrace{\delta(\alpha,\beta)}_{\substack{=0\\ \text{one spin is }\alpha,\\ \text{other spin is }\beta}}\sum_k \left[c^k(33,33)\right]^2 \underbrace{G^k(nf,nf)}_{\boxed{F^k(nf^2)}}$$

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

$$\left\langle {}^3H\left|\frac{e^2}{r_{12}}\right|{}^3H\right\rangle = \sum_{k=0,2,4,6}\left\{\left[c^k\overset{\boxed{e_1^-,e_1^-}}{\underset{\substack{\boxed{e_1^-}\\(\alpha,\alpha)}}{(33,33)}}\,c^k\overset{\boxed{e_2^-,e_2^-}}{\underset{\substack{\boxed{e_2^-}\\(\beta,\beta)}}{(32,32)}}\right]F^k(nf,nf) - \left[c^k\overset{\boxed{e_1^-,e_2^-}}{\underset{\text{both spins }\alpha}{(33,32)}}\right]^2 \underset{\llcorner\, F^k(nf^2)}{G^k(nf,nf)}\right\}$$

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!

	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	$-7/33$	$+[36/7361\bullet 64]^{1/2}$
$c^k(33,32)$	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

C&S Table: the number listed goes inside the SQRT replacing the numerator in the first row.

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 $[\ldots/D_k]^{1/2}$)

$$\left\langle {}^1I\left|\frac{e^2}{r_{12}}\right|{}^1I\right\rangle = F^0 + \left(\frac{1}{9}\right)F^2 + \left(\frac{1}{121}\right)F^4 + \left(\frac{1}{7361\cdot 64}\right)F^6$$
$$= F_0 + 25F_2 + 9F_4 + F_6$$

Always have the product of two factors of c^k. Thus $\mathrm{F^k}$ gets divided by $\mathrm{D_k}$ to yield $\mathrm{F_k}$.

$$\left\langle {}^3H\left|\frac{e^2}{r_{12}}\right|{}^3H\right\rangle = F^0 + \left[\left(-\frac{1}{3}\right)(0) - (1/3)^2\right]F^2 + \left[\left(\frac{1}{11}\right)\left(\frac{-7}{33}\right) - \frac{30}{33\cdot 33}\right]F^4 + \left[\frac{-6-7}{7361\cdot 64}\right]F^6$$
$$= F^0 - \frac{1}{9}F^2 - \frac{51}{(33)^2}F^4 \frac{-13}{7361\cdot 64}F^6$$
$$= F_0 - 25F_2 - 51F_4 - 13F_6$$

A lot of 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 ${}^3H$!

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: $\|3\alpha 0\alpha\|$ and $\|2\alpha 1\alpha\|$. This box generates $\left|{}^3H\, 31\right\rangle$ and $\left|{}^3F\, 31\right\rangle$, but the 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 exceptionally laborious, but it is much easier than:

- * generating each $|LM_L = L \;\; SM_S = S\rangle$ 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 $(nf)^2\,{}^{2S+1}L$ terms:

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

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

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

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

$$E^{(2)} = \left(\text{in}\underline{\text{tra}}\text{configuraional spin-orbit}\right) + \left(\text{in}\underline{\text{ter}}\text{configurational } e^2/r_{ij}\right)$$

Configuration Interaction

<u>For nf^2</u>

shielded by all filled subshells ↓ (to $2\varepsilon_{nf}$)

shielded by same subshell ↓ (to F_0)

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

shielded-core configurational energy (columns $2\varepsilon_{\mathrm{nf}} + F_0$)

intraconfiguration *L*-*S* term splittings (columns F_2, F_4, F_6)

(there is <u>NO</u> 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

   e.g. $d^3 \rightarrow$ two ${}^2D$ terms
   see pages 47-50 of Golding for 2 × 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

$$\text{e.g.}\qquad \text{nd}^2 \qquad {}^1S,{}^3P,{}^1D,{}^3F,{}^1G$$

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

choose any pair of orthogonal combinations of Slaters. What you choose determines the values of the off-diagonal matrix elements but not the eigen-energies

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!

5.73 Quantum Mechanics I
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