many-electron systems

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|r_i - r_{i'}|} - \sum_{i, \alpha} \frac{Z_\alpha}{|r_i - R_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|R_\alpha - R_{\alpha'}|} \]

how do we use group theory for many-body wavefunctions?
direct product wavefunctions

Slater determinants, combinations of Slater determinants

$$\frac{1}{\sqrt{N_e!}} \sum_P \text{sign}(P) \phi_{\alpha P_1}(r_1) \phi_{\alpha P_2}(r_2) \cdots \phi_{\alpha P_{N_e}}(r_{N_e})$$

use decomposition formula!

---

time-reversal symmetry

$N$-electrons with spin

$$\hat{T} = \sigma_{1y} \cdots \sigma_{Ny} \hat{K}$$

$$\hat{T} \Psi(r_1\sigma_1, \ldots, r_N\sigma_N) = (i)^{2(\sigma_1 + \cdots + \sigma_N)} \Psi^*(r_1 - \sigma_1, \ldots, r_N - \sigma_N)$$

$$T^2 = \pm 1$$

$N$ even: +1

$N$ odd: -1

$$[H, \hat{T}] = 0$$

$$H \Psi = E \Psi$$

$\hat{T} \Psi$ at least 2-fold degenerate
Kramers degeneracy

The energy levels of a system that contains an odd number of $S=1/2$ particles are at least doubly degenerated.

many-electron systems

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i, \alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \]

how do we use group theory for many-body wavefunctions?

how do we build many-body wavefunctions?
many electron systems

Pauli principle

we need permutation group S(n)

we have to select asymmetric representation

S(1)  one element, E
      one irr rep, symmetric

S(2)  two elements, E, A
      two irr reps, symmetric and asymmetric

atomic case and group O(3)

two-electron case

1s²  reps of S(2)

here orbital function (s s) is symmetric  Γ₁^s
need asymmetric spin function

Γ₁^a

²S  multiplet

S means total angular momentum is zero
atomic case and group O(3)

we can build orbitally symmetric and asymmetric functions

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1s^1)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(1p^1)</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(mm)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(mn)</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

for \(S(2)\) they are the only reps

rep for permutations of \((m,n)\) splits into

\[
\Gamma^a_1 + \Gamma^s_1
\]

atomic case and group O(3)

rep for permutations of \((m,n)\) splits into

\[
\Gamma^a_1 + \Gamma^s_1
\]

reps for spin 0 +1

\[
\Gamma^a_1 + \Gamma^s_1
\]

spin S=0 asymmetric

spin S=1, \(S_z=1\) symmetric

\(2^S\)

\(4^S\)
atomic multiplets

eigenstates of many-body atomic hamiltonian

$$2S+1 \quad \begin{array}{cc} L \mid J \end{array}$$

S: total spin
L: total angular momentum
J: total total angular momentum

atomic case and group O(3)

three-electron case

S(3) isomorphic to C\textsubscript{3v}

three irreducible reps

<table>
<thead>
<tr>
<th>S(3)</th>
<th>E</th>
<th>A, B, C</th>
<th>D, F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1^a$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_1^s$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>2</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>($\phi_m \phi_m \phi_m$)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>($\phi_m \phi_m \phi_p$)</td>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>($\phi_m \phi_p \phi_q$)</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$\Gamma_1^a + \Gamma_1^s + 2\Gamma_2$
three-electron case

spin states

\[ (\sigma\sigma\sigma) \quad \Gamma_1^s \]
\[ (\sigma\sigma - \sigma) \quad \Gamma_1^s + \Gamma_2 \]

atomic case and group O(3)

three-electron case

\begin{align*}
1s^3 & \quad \text{no} \quad \Gamma_1^a \quad \text{not allowed} \\
1s^2 2s^1 & \quad 2S \quad L=0 \quad S=1/2 \\
1s^2 2p^1 & \quad 2P \quad L=1 \quad S=1/2
\end{align*}
atomic limit and group $O(h)$

atomic Hamiltonian + crystal-field

Example $l=2$ shell configuration $t_{2g}^6e_{g}^n$

for the $t_{2g}^6$ state we have total spin zero $S=0$ and symmetric function

for the $e_{2g}^n$ state

$\begin{align*}
  n=2 & \quad (\phi_m \phi_n) \quad (\phi_m \phi_m) \\
  n=3 & \quad (\phi_m \phi_m \phi_n) \quad (\phi_m \phi_n \phi_n)
\end{align*}$

wavefunctions can then be build with the projectors

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