Addition of the spin angular momentum of three (four) electrons with S = 1/2

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Here we show how to derive the eigenvalues and eigenkets of $\hat{\boldsymbol{S}}^2$, the spin states of the three and four electrons with spin 1/2, where $\hat{\boldsymbol{S}}$ is the total spin angular momentum defined by

$$\hat{\boldsymbol{S}} = \hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2 + \hat{\boldsymbol{S}}_3, \qquad \text{for the three particles}$$

$$\hat{\boldsymbol{S}} = \hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2 + \hat{\boldsymbol{S}}_3 + \hat{\boldsymbol{S}}_4. \qquad \text{for the four particles}$$

There are two methods. One is the conventional method to use the Clebsch-Gordan coefficients for the addition of spin angular momentum. Using the program of ClebschGordan (Mathematica), we can derive the expression for the eigenket and eigenvalues for $\hat{\boldsymbol{S}}^2$ for the many spin particles. The second method is to use the KroneckerProduct of the Mathematica for both the three and four spins. We calculate the expression of the matrix for $\hat{\boldsymbol{S}}^2$; 8x8 matrix for the three spin particles and 16x16 matrix for the four spin particles. Using the Mathematica we solve the eigenvalue problems to get the eigenvalues and eigenkets for each case. We can also solve the eigenvalue problem even for the five spin particles, the 32x32 martix by using the Mathematica.

Note that for the *n* particle systems, we need to solve the eigenvalue problem for 2^nx2^n martix (*n* = 2, 3, 4, 5, 6, ...).

1. States of three particles with spin 1/2 (I)

We can regard three electrons as 2+1 electrons, in the sense that we can combine an electron (s = 1/2) with the triplet two-electron state (*s* = 1) and with the singlet two-electron state (*s* = 0).

$$D_{1/2} \times D_{1/2} = D_1 + D_0 .$$

((Case-1))

$$\begin{aligned} D_{1/2} \times D_{1/2} \times D_{1/2} &= (D_{1/2} \times D_{1/2}) \times D_{1/2} \\ &= (D_1 + D_0) \times D_{1/2} \\ &= D_1 \times D_{1/2} + D_0 \times D_{1/2} \\ &= D_{3/2} + D_{1/2} + D_{1/2} \end{aligned}$$

In the case of $(D_{3/2} + D_{1/2})$, the results on the addition of the angular momenta shows that we should get two groups of three-electron spin states corresponding to *S* = 3/2 and *S* = 1/2. In the second case we get a single group that corresponds to S = 1/2. We thus expect one quartet group of spin states (S = 3/2) and two distinct doublet groups of spin states (S = 1/2), or a total of 4+2+2 = 8 individual three-electron spin states.

(1) j = 3/2.

$$\left|\frac{3}{2},-\frac{3}{2}\right\rangle = \beta(1)\beta(2)\beta(3)\,,$$

$$\left|\frac{3}{2},-\frac{1}{2}\right\rangle = \frac{\alpha(1)\beta(2)\beta(3)+\beta(1)\alpha(2)\beta(3)+\beta(1)\beta(2)\alpha(3)}{\sqrt{3}}$$

$$\left|\frac{3}{2},\frac{1}{2}\right\rangle = \frac{\beta(1)\alpha(2)\alpha(3)+\alpha(1)\beta(2)\alpha(3)+\alpha(1)\alpha(2)\beta(3)}{\sqrt{3}}$$

$$\left|\frac{3}{2},\frac{3}{2}\right\rangle = \alpha(1)\alpha(2)\alpha(3)$$

(ii) j = 1/2.

$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle = \frac{\alpha(1)\beta(2)\beta(3)+\beta(1)\alpha(2)\beta(3)-2\beta(1)\beta(2)\alpha(3)}{\sqrt{6}}$$

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle = \frac{-\beta(1)\alpha(2)\alpha(3)+2\alpha(1)\alpha(2)\beta(3)-\alpha(1)\beta(2)\alpha(3)}{\sqrt{6}}$$

(iii) j = 1/2

$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle = \frac{\alpha(1)\beta(2)\beta(3)-\beta(1)\alpha(2)\beta(3)}{\sqrt{2}}$$

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle = \frac{\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3)}{\sqrt{2}}$$

Note that α and β denote the upper spin state and the lower spin state, respectively;

$$\alpha = |+z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \beta = |-z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

The numbers 1, 2, and 3 are the sites of spins. These results are the same as those derived by Tomonaga, except for the sign.

((Mathematica-1))

```
Clear["Global`*"]; CCGG[{j1_, m1_}, {j2_, m2_}, {j_, m_}] :=
 Module[{s1},
  s1 = If[Abs[m1] ≤ j1 && Abs[m2] ≤ j2 && Abs[m] ≤ j,
    ClebschGordan[{j1, m1}, {j2, m2}, {j, m}], 0]];

CG2[j1_, j2_, j_, a1_, a2_] :=
 Table[Sum[CCGG[{j1, k1}, {j2, k2}, {j, k1 + k2}] a1[j1, k1] a2[j2, k2]
    KroneckerDelta[k1 + k2, m], {k1, -j1, j1}, {k2, -j2, j2}], {m, -j, j}]
```

j1=1/2, j2=1/2 j = 1, 0

```
CG2[1/2, 1/2, 1, b1, b2] // TableForm
```

$$b1\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] b2\left[\tfrac{1}{2}, -\tfrac{1}{2}\right]$$
$$\frac{b1\left[\tfrac{1}{2},\tfrac{1}{2}\right] b2\left[\tfrac{1}{2},-\tfrac{1}{2}\right]}{\sqrt{2}} + \frac{b1\left[\tfrac{1}{2},-\tfrac{1}{2}\right] b2\left[\tfrac{1}{2},\tfrac{1}{2}\right]}{\sqrt{2}}$$
$$b1\left[\tfrac{1}{2}, \tfrac{1}{2}\right] b2\left[\tfrac{1}{2}, \tfrac{1}{2}\right]$$

```
CG2[1/2, 1/2, 0, b1, b2] // TableForm
```

$$\frac{b1\left[\tfrac{1}{2},\tfrac{1}{2}\right] b2\left[\tfrac{1}{2},-\tfrac{1}{2}\right]}{\sqrt{2}} - \frac{b1\left[\tfrac{1}{2},-\tfrac{1}{2}\right] b2\left[\tfrac{1}{2},\tfrac{1}{2}\right]}{\sqrt{2}}$$

j1=1, j2=1/2 j = 3/2

```
j1 = 1; j2 = 1/2; j = 3/2;
Table[Sum[CCGG[{j1, k1}, {j2, k2}, {j, k1 + k2}] CG2[1/2, 1/2, j1, b1, b2][[k1 + j1 + 1]]
    b3[j2, k2] KroneckerDelta[k1 + k2, m], {k1, -j1, j1}, {k2, -j2, j2}], {m, -j, j}] //
 Simplify
```

$$\Big\{b1\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] b2\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] b3\left[\tfrac{1}{2}, -\tfrac{1}{2}\right],$$
$$\frac{b1\left[\tfrac{1}{2}, \tfrac{1}{2}\right] b2\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] b3\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] + b1\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] \left(b2\left[\tfrac{1}{2}, \tfrac{1}{2}\right] b3\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] + b2\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] b3\left[\tfrac{1}{2}, \tfrac{1}{2}\right]\right)}{\sqrt{3}},$$
$$\frac{b1\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] b2\left[\tfrac{1}{2}, \tfrac{1}{2}\right] b3\left[\tfrac{1}{2}, \tfrac{1}{2}\right] + b1\left[\tfrac{1}{2}, \tfrac{1}{2}\right] \left(b2\left[\tfrac{1}{2}, \tfrac{1}{2}\right] b3\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] + b2\left[\tfrac{1}{2}, -\tfrac{1}{2}\right] b3\left[\tfrac{1}{2}, \tfrac{1}{2}\right]\right)}{\sqrt{3}},$$
$$b1\left[\tfrac{1}{2}, \tfrac{1}{2}\right] b2\left[\tfrac{1}{2}, \tfrac{1}{2}\right] b3\left[\tfrac{1}{2}, \tfrac{1}{2}\right]\Big\}$$

j1=1, j2=1/2 j = 1/2

```
j1 = 1; j2 = 1/2; j = 1/2;
Table[Sum[CCGG[{j1, k1}, {j2, k2}, {j, k1 + k2}] CG2[1/2, 1/2, j1, b1, b2][[k1 + j1 + 1]]
   b3[j2, k2] KroneckerDelta[k1 + k2, m], {k1, -j1, j1}, {k2, -j2, j2}], {m, -j, j}] //
 Simplify
```

$$\left\{\frac{b1\left[\frac{1}{2},\frac{1}{2}\right] b2\left[\frac{1}{2},-\frac{1}{2}\right] b3\left[\frac{1}{2},-\frac{1}{2}\right]+b1\left[\frac{1}{2},-\frac{1}{2}\right]\left(b2\left[\frac{1}{2},\frac{1}{2}\right] b3\left[\frac{1}{2},-\frac{1}{2}\right]-2\, b2\left[\frac{1}{2},-\frac{1}{2}\right] b3\left[\frac{1}{2},\frac{1}{2}\right]\right)}{\sqrt{6}},\right.$$
$$\left.\frac{-b1\left[\frac{1}{2},-\frac{1}{2}\right] b2\left[\frac{1}{2},\frac{1}{2}\right] b3\left[\frac{1}{2},\frac{1}{2}\right]+b1\left[\frac{1}{2},\frac{1}{2}\right]\left(2\, b2\left[\frac{1}{2},\frac{1}{2}\right] b3\left[\frac{1}{2},-\frac{1}{2}\right]-b2\left[\frac{1}{2},-\frac{1}{2}\right] b3\left[\frac{1}{2},\frac{1}{2}\right]\right)}{\sqrt{6}}\right\}$$

j1=0, j2=1/2 j = 1/2

```
j1 = 0; j2 = 1/2; j = 1/2;
Table[Sum[CCGG[{j1, k1}, {j2, k2}, {j, k1 + k2}] CG2[1/2, 1/2, j1, b1, b2][[k1 + j1 + 1]]
   b3[j2, k2] KroneckerDelta[k1 + k2, m], {k1, -j1, j1}, {k2, -j2, j2}], {m, -j, j}] //
 Simplify
```

$$\left\{\frac{\left(b1\left[\frac{1}{2},\frac{1}{2}\right] b2\left[\frac{1}{2},-\frac{1}{2}\right]-b1\left[\frac{1}{2},-\frac{1}{2}\right] b2\left[\frac{1}{2},\frac{1}{2}\right]\right) b3\left[\frac{1}{2},-\frac{1}{2}\right]}{\sqrt{2}},\right.$$
$$\left.\frac{\left(b1\left[\frac{1}{2},\frac{1}{2}\right] b2\left[\frac{1}{2},-\frac{1}{2}\right]-b1\left[\frac{1}{2},-\frac{1}{2}\right] b2\left[\frac{1}{2},\frac{1}{2}\right]\right) b3\left[\frac{1}{2},\frac{1}{2}\right]}{\sqrt{2}}\right\}$$

2. States of three particles with spin 1/2 (II)

We consider the second case. The results on the spin states are the same as those described in the textbook of Schiff.

$$\begin{aligned} D_{1/2}\times D_{1/2}\times D_{1/2} &= D_{1/2}\times(D_{1/2}\times D_{1/2}) \\ &= D_{1/2}\times(D_1+D_0) \\ &= D_{1/2}\times D_1 + D_{1/2}\times D_0 \\ &= D_{3/2}+D_{1/2}+D_{1/2} \end{aligned}$$

(1) $j = 3/2$.

$$\left|\frac{3}{2},-\frac{3}{2}\right\rangle = \beta(1)\beta(2)\beta(3),$$

$$\left|\frac{3}{2},-\frac{1}{2}\right\rangle = \frac{\alpha(1)\beta(2)\beta(3)+\beta(1)\alpha(2)\beta(3)+\beta(1)\beta(2)\alpha(3)}{\sqrt{3}},$$

$$\left|\frac{3}{2},\frac{1}{2}\right\rangle = \frac{\beta(1)\alpha(2)\alpha(3)+\alpha(1)\alpha(2)\beta(3)+\alpha(1)\beta(2)\alpha(3)}{\sqrt{3}},$$

$$\left|\frac{3}{2},\frac{3}{2}\right\rangle = \alpha(1)\alpha(2)\alpha(3) .$$

(ii) $j = 1/2$.

$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle = \frac{-2\alpha(1)\beta(2)\beta(3) + \beta(1)\alpha(2)\beta(3) + \beta(1)\beta(2)\alpha(3)}{\sqrt{6}} ,$$

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle = \frac{2\beta(1)\alpha(2)\alpha(3) - \alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\alpha(3)}{\sqrt{6}} .$$

(iii) $j = 1/2$

$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle = \frac{\beta(1)\alpha(2)\beta(3) - \beta(1)\beta(2)\alpha(3)}{\sqrt{2}} ,$$

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle = \frac{\alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\beta(3)}{\sqrt{2}} .$$

((**Mathematica-2**))

```
Clear["Global`*"]; CCGG[{j1_, m1_}, {j2_, m2_}, {j_, m_}] :=
 Module[{s1},
  s1 = If[Abs[m1] ≤ j1 && Abs[m2] ≤ j2 && Abs[m] ≤ j,
    ClebschGordan[{j1, m1}, {j2, m2}, {j, m}], 0]];

CG2[j1_, j2_, j_, a1_, a2_] :=
 Table[Sum[CCGG[{j1, k1}, {j2, k2}, {j, k1 + k2}] a1[j1, k1] a2[j2, k2]
    KroneckerDelta[k1 + k2, m], {k1, -j1, j1}, {k2, -j2, j2}], {m, -j, j}]
```

j1=1/2, j2=1/2 j = 1, 0

```
CG2[1/2, 1/2, 1, b1, b2] // TableForm
```

$$b1\left[\frac{1}{2}, -\frac{1}{2}\right] b2\left[\frac{1}{2}, -\frac{1}{2}\right]$$

$$\frac{b1\left[\frac{1}{2},\frac{1}{2}\right] b2\left[\frac{1}{2},-\frac{1}{2}\right]}{\sqrt{2}} + \frac{b1\left[\frac{1}{2},-\frac{1}{2}\right] b2\left[\frac{1}{2},\frac{1}{2}\right]}{\sqrt{2}}$$

$$b1\left[\frac{1}{2}, \frac{1}{2}\right] b2\left[\frac{1}{2}, \frac{1}{2}\right]$$

```
CG2[1/2, 1/2, 0, b1, b2] // TableForm
```

$$\frac{b1\left[\frac{1}{2},\frac{1}{2}\right] b2\left[\frac{1}{2},-\frac{1}{2}\right]}{\sqrt{2}} - \frac{b1\left[\frac{1}{2},-\frac{1}{2}\right] b2\left[\frac{1}{2},\frac{1}{2}\right]}{\sqrt{2}}$$

j1=1, j2=1/2 j = 3/2

```
j1 = 1; j2 = 1/2; j = 3/2;
Table[Sum[b1[j2, k2] CCGG[{j1, k1}, {j2, k2}, {j, k1 + k2}]
    CG2[1/2, 1/2, j1, b2, b3][[k1 + j1 + 1]] KroneckerDelta[k1 + k2, m],
   {k1, -j1, j1}, {k2, -j2, j2}], {m, -j, j}] // Simplify
```

$$\Big\{b1\left[\frac{1}{2}, -\frac{1}{2}\right] b2\left[\frac{1}{2}, -\frac{1}{2}\right] b3\left[\frac{1}{2}, -\frac{1}{2}\right],$$

$$\frac{b1\left[\frac{1}{2}, \frac{1}{2}\right] b2\left[\frac{1}{2}, -\frac{1}{2}\right] b3\left[\frac{1}{2}, -\frac{1}{2}\right] + b1\left[\frac{1}{2}, -\frac{1}{2}\right] \left(b2\left[\frac{1}{2}, \frac{1}{2}\right] b3\left[\frac{1}{2}, -\frac{1}{2}\right] + b2\left[\frac{1}{2}, -\frac{1}{2}\right] b3\left[\frac{1}{2}, \frac{1}{2}\right]\right)}{\sqrt{3}},$$

$$\frac{b1\left[\frac{1}{2}, -\frac{1}{2}\right] b2\left[\frac{1}{2}, \frac{1}{2}\right] b3\left[\frac{1}{2}, \frac{1}{2}\right] + b1\left[\frac{1}{2}, \frac{1}{2}\right] \left(b2\left[\frac{1}{2}, \frac{1}{2}\right] b3\left[\frac{1}{2}, -\frac{1}{2}\right] + b2\left[\frac{1}{2}, -\frac{1}{2}\right] b3\left[\frac{1}{2}, \frac{1}{2}\right]\right)}{\sqrt{3}},$$

$$b1\left[\frac{1}{2}, \frac{1}{2}\right] b2\left[\frac{1}{2}, \frac{1}{2}\right] b3\left[\frac{1}{2}, \frac{1}{2}\right]\Big\}$$

j1=1, j2=1/2 j = 1/2

```
j1 = 1; j2 = 1/2; j = 1/2;
Table[Sum[b1[j2, k2] CCGG[{j1, k1}, {j2, k2}, {j, k1 + k2}]
    CG2[1/2, 1/2, j1, b2, b3][[k1 + j1 + 1]] KroneckerDelta[k1 + k2, m],
   {k1, -j1, j1}, {k2, -j2, j2}], {m, -j, j}] // Simplify
```

$$\left\{\frac{-2\,\text{b1}[\frac{1}{2},\frac{1}{2}]\,\text{b2}[\frac{1}{2},-\frac{1}{2}]\,\text{b3}[\frac{1}{2},-\frac{1}{2}]+\text{b1}[\frac{1}{2},-\frac{1}{2}]\,(\text{b2}[\frac{1}{2},\frac{1}{2}]\,\text{b3}[\frac{1}{2},-\frac{1}{2}]+\text{b2}[\frac{1}{2},-\frac{1}{2}]\,\text{b3}[\frac{1}{2},\frac{1}{2}])}{\sqrt{6}},\right.$$
$$\left.\frac{2\,\text{b1}[\frac{1}{2},-\frac{1}{2}]\,\text{b2}[\frac{1}{2},\frac{1}{2}]\,\text{b3}[\frac{1}{2},\frac{1}{2}]-\text{b1}[\frac{1}{2},\frac{1}{2}]\,(\text{b2}[\frac{1}{2},\frac{1}{2}]\,\text{b3}[\frac{1}{2},-\frac{1}{2}]+\text{b2}[\frac{1}{2},-\frac{1}{2}]\,\text{b3}[\frac{1}{2},\frac{1}{2}])}{\sqrt{6}}\right\}$$

j1=0, j2=1/2 j = 1/2

```
j1 = 0; j2 = 1/2; j = 1/2;
Table[Sum[b1[j2, k2] CCGG[{j1, k1}, {j2, k2}, {j, k1 + k2}]
    CG2[1/2, 1/2, j1, b2, b3][[k1 + j1 + 1]] KroneckerDelta[k1 + k2, m],
   {k1, -j1, j1}, {k2, -j2, j2}], {m, -j, j}] // Simplify
```

$$\left\{\frac{\text{b1}[\frac{1}{2},-\frac{1}{2}]\,(\text{b2}[\frac{1}{2},\frac{1}{2}]\,\text{b3}[\frac{1}{2},-\frac{1}{2}]-\text{b2}[\frac{1}{2},-\frac{1}{2}]\,\text{b3}[\frac{1}{2},\frac{1}{2}])}{\sqrt{2}},\right.$$
$$\left.\frac{\text{b1}[\frac{1}{2},\frac{1}{2}]\,(\text{b2}[\frac{1}{2},\frac{1}{2}]\,\text{b3}[\frac{1}{2},-\frac{1}{2}]-\text{b2}[\frac{1}{2},-\frac{1}{2}]\,\text{b3}[\frac{1}{2},\frac{1}{2}])}{\sqrt{2}}\right\}$$

3. The three spin states (by the use of KroneckerProduct)

The magnitude of the total spin angular momentum:

$$\hat{\boldsymbol{S}}^2 = \frac{\hbar^2}{4}(\hat{\boldsymbol{\sigma}}_1 + \hat{\boldsymbol{\sigma}}_2 + \hat{\boldsymbol{\sigma}}_3)^2$$
$$= \frac{\hbar^2}{4}(\hat{\boldsymbol{\sigma}}_1{}^2 + \hat{\boldsymbol{\sigma}}_2{}^2 + \hat{\boldsymbol{\sigma}}_3{}^2 + 2\hat{\boldsymbol{\sigma}}_1\cdot\hat{\boldsymbol{\sigma}}_2 + 2\hat{\boldsymbol{\sigma}}_2\cdot\hat{\boldsymbol{\sigma}}_3 + 2\hat{\boldsymbol{\sigma}}_3\cdot\hat{\boldsymbol{\sigma}}_1)$$
$$= \frac{9\hbar^2}{4}\hat{1} + \frac{\hbar^2}{2}(\hat{\boldsymbol{\sigma}}_1\cdot\hat{\boldsymbol{\sigma}}_2 + \hat{\boldsymbol{\sigma}}_2\cdot\hat{\boldsymbol{\sigma}}_3 + \hat{\boldsymbol{\sigma}}_3\cdot\hat{\boldsymbol{\sigma}}_1)$$

and the *z*-component of the total spin angular momentum:

$$\hat{S}_z = \frac{\hbar}{2}(\hat{\sigma}_{1z} + \hat{\sigma}_{2z} + \hat{\sigma}_{2z}).$$

Using thr Kronecker product, the above operators can be rewritten as

$$\hat{\boldsymbol{S}}^2 \to \frac{9\hbar^2}{4}\hat{1}\otimes\hat{1}\otimes\hat{1} + \frac{\hbar^2}{2}(\hat{\sigma}_x\otimes\hat{\sigma}_x\otimes\hat{1} + \hat{\sigma}_y\otimes\hat{\sigma}_y\otimes\hat{1} + \hat{\sigma}_z\otimes\hat{\sigma}_z\otimes\hat{1}$$
$$+\hat{\sigma}_x\otimes\hat{1}\otimes\hat{\sigma}_x + \hat{\sigma}_y\otimes\hat{1}\otimes\hat{\sigma}_y + \hat{\sigma}_z\otimes\hat{1}\otimes\hat{\sigma}_z$$
$$+\otimes\hat{1}\hat{\sigma}_x\otimes\hat{\sigma}_x + \otimes\hat{1}\hat{\sigma}_y\otimes\hat{\sigma}_y + \otimes\hat{1}\hat{\sigma}_z\otimes\hat{\sigma}_z)$$

$$\hat{S}_z \to \frac{\hbar}{2}(\hat{\sigma}_z\otimes\hat{1}\otimes\hat{1} + \hat{1}\otimes\hat{\sigma}_z\otimes\hat{1} + \hat{1}\otimes\hat{1}\otimes\hat{\sigma}_z).$$

The matrix of $\hat{\boldsymbol{S}}^2$ is obtained with the use of KrocknerProduct in the Mathematica, as

$$\begin{pmatrix} \frac{15}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{7}{4} & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & \frac{7}{4} & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{7}{4} & 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 & \frac{7}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & \frac{7}{4} & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & \frac{7}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{15}{4} \end{pmatrix}$$

The matrix of $\hat{S}_z$ is obtained as

$$\begin{pmatrix} \frac{3}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{3}{2} \end{pmatrix}$$

Note that $\hat{S}_z$ is the block-diagonnal matrix,but $\hat{\boldsymbol{S}}^2$ is a non-diagonal matrix.

The eigenvalue problem of $\hat{\boldsymbol{S}}^2$. We use the Eigensystem (Mathematica) to solve the eigenvalue problem. The result is as follows: {eigenvalues, eigenkets}}

```
{{{15/4, 15/4, 15/4, 15/4, 3/4, 3/4, 3/4, 3/4},
 {{0, 0, 0, 0, 0, 0, 0, 1}, {0, 0, 0, 1, 0, 1, 1, 0}, {0, 1, 1, 0, 1, 0, 0, 0},
  {1, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, -1, 0, 0, 1, 0}, {0, 0, 0, -1, 0, 1, 0, 0},
  {0, -1, 0, 0, 1, 0, 0, 0}, {0, -1, 1, 0, 0, 0, 0, 0}}}
```

The eigenkets of $\hat{\boldsymbol{S}}^2$

(a)

$$\left| j=\frac{2}{3}, m=\frac{3}{2}\right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \qquad \left| j=\frac{3}{2}, m=\frac{1}{2}\right\rangle = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ 0 \\ \frac{1}{\sqrt{3}} \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\left| j=\frac{3}{2}, m=-\frac{1}{2}\right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{\sqrt{3}} \\ 0 \\ \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ 0 \end{pmatrix}, \qquad \left| j=\frac{3}{2}, m=-\frac{3}{2}\right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix},$$

(b) $j = 1/2$

$$\left| j=\frac{1}{2}, m=-\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{\sqrt{2}} \\ 0 \\ 0 \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}, \qquad \left| j=\frac{1}{2}, m=\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ 0 \\ 0 \\ \frac{1}{\sqrt{2}} \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

(c) j = 1/2

$$\left| j=\frac{1}{2}, m=\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{6}} \\ -\frac{2}{\sqrt{6}} \\ 0 \\ \frac{1}{\sqrt{6}} \\ 0 \\ 0 \\ 0 \end{pmatrix}, \qquad \left| j=\frac{1}{2}, m=-\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{\sqrt{6}} \\ 0 \\ -\frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{6}} \\ 0 \end{pmatrix}$$

4. The four-spin states (by the use of KroneckerProduct)

We now consider the eigenstates and eigenvalues for the four-spin system.

$$\begin{aligned} D_{1/2} \times D_{1/2} \times D_{1/2} \times D_{1/2} &= (D_{1/2} \times D_{1/2}) \times (D_{1/2} \times D_{1/2}) \\ &= (D_1 + D_0) \times (D_1 + D_0) \\ &= D_1 \times D_1 + D_1 \times D_0 + D_0 \times D_1 + D_0 \times D_0 \\ &= (D_2 + D_1 + D_0) + D_1 + D_1 + D_0 \\ &= D_2 + 3D_1 + 2D_0 \end{aligned}$$

The total states are 16 states (= 5 + 3 x 3+2), since

j = 2	m = 2, 1, 0, -1, -2	(one)	1 x 5 = 5
j = 1	m = 1, 0, -1	(three)	3 x 3 = 9
j = 0	m = 0.	(two)	2 x 2 = 4

The square of the magnitude of the total spin angular momentum

$$
\begin{aligned}
\hat{\boldsymbol{S}}^2 &= \frac{\hbar^2}{4}(\hat{\boldsymbol{\sigma}}_1 + \hat{\boldsymbol{\sigma}}_2 + \hat{\boldsymbol{\sigma}}_3 + \hat{\boldsymbol{\sigma}}_4)^2 \\
&= \frac{\hbar^2}{4}(\hat{\boldsymbol{\sigma}}_1{}^2 + \hat{\boldsymbol{\sigma}}_2{}^2 + \hat{\boldsymbol{\sigma}}_3{}^2 + \hat{\boldsymbol{\sigma}}_4{}^2 + 2\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2 + 2\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_3 + 2\hat{\boldsymbol{\sigma}}_2 \cdot \hat{\boldsymbol{\sigma}}_3 + \\
&\quad + 2\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_4 + 2\hat{\boldsymbol{\sigma}}_2 \cdot \hat{\boldsymbol{\sigma}}_4 + 2\hat{\boldsymbol{\sigma}}_3 \cdot \hat{\boldsymbol{\sigma}}_4) \\
&= 3\hbar^2\hat{1} + \frac{\hbar^2}{2}(\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2 + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_3 + \hat{\boldsymbol{\sigma}}_2 \cdot \hat{\boldsymbol{\sigma}}_3 + \\
&\quad + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_4 + \hat{\boldsymbol{\sigma}}_2 \cdot \hat{\boldsymbol{\sigma}}_4 + \hat{\boldsymbol{\sigma}}_3 \cdot \hat{\boldsymbol{\sigma}}_4)
\end{aligned}
$$

The *z* component of the spin angular momentum:

$$
\hat{S}_z = \frac{\hbar}{2}(\hat{\sigma}_{1z} + \hat{\sigma}_{2z} + \hat{\sigma}_{3z} + \hat{\sigma}_{4z})
$$

These operators can be rewritten as

$$
\begin{aligned}
\hat{\boldsymbol{S}}^2 \to 3\hbar^2\hat{1}\otimes\hat{1}\otimes\hat{1}\otimes\hat{1} + \frac{\hbar^2}{2}(&\hat{\sigma}_x \otimes \hat{\sigma}_x \otimes \hat{1}\otimes\hat{1} + \hat{\sigma}_y \otimes \hat{\sigma}_y \otimes \hat{1}\otimes\hat{1} + \hat{\sigma}_z \otimes \hat{\sigma}_z \otimes \hat{1}\otimes\hat{1} \\
&+ \hat{\sigma}_x \otimes \hat{1}\otimes \hat{\sigma}_x \otimes \hat{1} + \hat{\sigma}_y \otimes \hat{1}\otimes \hat{\sigma}_y \otimes \hat{1} + \hat{\sigma}_z \otimes \hat{1}\otimes \hat{\sigma}_z \otimes \hat{1} \\
&+ \hat{1}\otimes \hat{\sigma}_x \otimes \hat{\sigma}_x \otimes \hat{1} + \hat{1}\otimes \hat{\sigma}_y \otimes \hat{\sigma}_y \otimes \hat{1} + \otimes\hat{1}\hat{\sigma}_z \otimes \hat{\sigma}_z \otimes \hat{1} \\
&+ \hat{\sigma}_x \otimes \hat{1}\otimes\hat{1}\otimes \hat{\sigma}_x + \hat{\sigma}_y \otimes \hat{1}\otimes\hat{1}\otimes \hat{\sigma}_y + \hat{\sigma}_z \otimes \hat{1}\otimes\hat{1}\otimes \hat{\sigma}_z \\
&+ \hat{1}\otimes \hat{\sigma}_x \otimes \hat{1}\otimes \hat{\sigma}_x + \hat{1}\otimes \hat{\sigma}_y \otimes \hat{1}\otimes \hat{\sigma}_y + \hat{1}\otimes \hat{\sigma}_z \otimes \hat{1}\otimes \hat{\sigma}_z \\
&+ \hat{1}\otimes\hat{1}\otimes \hat{\sigma}_x \otimes \hat{\sigma}_x + \hat{1}\otimes\hat{1}\otimes \hat{\sigma}_y \otimes \hat{\sigma}_y + \hat{1}\otimes\hat{1}\otimes \hat{\sigma}_z \otimes \hat{\sigma}_z)
\end{aligned}
$$

and

$$
\hat{S}_z \to \frac{\hbar}{2}(\hat{\sigma}_z \otimes \hat{1}\otimes\hat{1} + \hat{1}\otimes \hat{\sigma}_z \otimes \hat{1} + \hat{1}\otimes\hat{1}\otimes \hat{\sigma}_z)
$$

Using the Mathematica we can solve the eigenvalue problems for the four spin 1/2 systems. The matrix of $\hat{\boldsymbol{S}}^2$ (16 x 16 matrix) is expressed by

$$
\begin{pmatrix}
6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 3 & 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 3 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 2 & 0 & 1 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 1 & 0 & 3 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 2 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 2 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 \\
0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 2 & 1 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 2 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 3 & 0 & 1 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 1 & 0 & 2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 3 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 3 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6
\end{pmatrix}
$$

The matrix of $\hat{S}_z$ (16 x 16 matrix) is expressed as

$$
\begin{pmatrix}
2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2
\end{pmatrix}
$$

The eigenvalue problem of $\hat{\boldsymbol{S}}^2$

(a) $j = 2$

$$\left| j=2,m=2\right\rangle =\begin{pmatrix}1\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\\0\end{pmatrix},\qquad \left| j=2,m=1\right\rangle =\begin{pmatrix}0\\1/2\\1/2\\0\\1/2\\0\\0\\0\\1/2\\0\\0\\0\\0\\0\\0\\0\end{pmatrix}$$

$$\left| j=2,m=0\right\rangle =\begin{pmatrix}0\\0\\0\\1/\sqrt{6}\\0\\1/\sqrt{6}\\1/\sqrt{6}\\0\\0\\1/\sqrt{6}\\1/\sqrt{6}\\0\\1/\sqrt{6}\\0\\0\\0\end{pmatrix}\qquad \left| j=2,m=-1\right\rangle =\begin{pmatrix}0\\0\\0\\0\\0\\0\\0\\1/2\\0\\0\\0\\1/2\\0\\1/2\\1/2\\0\end{pmatrix}$$

$$\left| j=2, m=-2 \right\rangle == \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

(b)

$$\left| j=1, m=1 \right\rangle = \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \left| j=1, m=1 \right\rangle = \begin{pmatrix} 0 \\ 1/\sqrt{6} \\ 0 \\ 0 \\ -2/\sqrt{6} \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{6} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \left| j=1, m=1 \right\rangle = \begin{pmatrix} 0 \\ \sqrt{3}/6 \\ -\sqrt{3}/2 \\ 0 \\ \sqrt{3}/6 \\ 0 \\ 0 \\ 0 \\ \sqrt{3}/6 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\left| j=1, m=0 \right\rangle == \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1/\sqrt{2} \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \left| j=1, m=0 \right\rangle == \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ -1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \left| j=1, m=0 \right\rangle == \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ 0 \\ 0 \\ -1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\left| j=1, m=-1 \right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1/\sqrt{2} \\ 0 \end{pmatrix} \quad \left| j=1, m=-1 \right\rangle == \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{6} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -2/\sqrt{6} \\ 1/\sqrt{6} \\ 0 \end{pmatrix} \quad \left| j=1, m=-1 \right\rangle == \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \sqrt{3}/6 \\ 0 \\ 0 \\ 0 \\ -\sqrt{3}/2 \\ 0 \\ \sqrt{3}/6 \\ \sqrt{3}/6 \\ 0 \end{pmatrix}$$

$$\left| j=0, m=0 \right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1/2 \\ 0 \\ 0 \\ -1/2 \\ 0 \\ 0 \\ -1/2 \\ 0 \\ 0 \\ 1/2 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

(

$$\left| j=0, m=0 \right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \sqrt{3}/6 \\ 0 \\ -1/\sqrt{3} \\ \sqrt{3}/6 \\ 0 \\ 0 \\ \sqrt{3}/6 \\ -1/\sqrt{3} \\ 0 \\ \sqrt{3}/6 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

((**Mathematica**))

```
Clear["Global`*"];
exp_* := exp /. {Complex[re_, im_] :> Complex[re, -im]}; σx = (0  1
                                                              1  0);
σy = (0  -ⅈ
      ⅈ   0); σz = (1   0
                    0  -1);
I2 = IdentityMatrix[2];

ST1 = 1/2 (KroneckerProduct[σx, σx, I2, I2] + KroneckerProduct[σy, σy, I2, I2]
       + KroneckerProduct[σz, σz, I2, I2] + KroneckerProduct[σx, I2, σx, I2] +
       KroneckerProduct[σy, I2, σy, I2] + KroneckerProduct[σz, I2, σz, I2] +
       KroneckerProduct[σx, I2, I2, σx] + KroneckerProduct[σy, I2, I2, σy] +
       KroneckerProduct[σz, I2, I2, σz] + KroneckerProduct[I2, σx, σx, I2] +
       KroneckerProduct[I2, σy, σy, I2] + KroneckerProduct[I2, σz, σz, I2] +
       KroneckerProduct[I2, I2, σx, σx] + KroneckerProduct[I2, I2, σy, σy] +
       KroneckerProduct[I2, I2, σz, σz] + KroneckerProduct[I2, σx, I2, σx] +
       KroneckerProduct[ I2, σy, I2, σy] + KroneckerProduct[I2, σz, I2, σz]) +
    3 KroneckerProduct[I2, I2, I2, I2];
ST1 // MatrixForm
```

$$
\begin{pmatrix}
6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 3 & 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 3 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 2 & 0 & 1 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 1 & 0 & 3 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 2 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 2 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 \\
0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 2 & 1 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 2 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 3 & 0 & 1 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 1 & 0 & 2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 3 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 3 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6
\end{pmatrix}
$$

```
eq1 = Eigensystem[ST1] // Simplify

{{6, 6, 6, 6, 6, 2, 2, 2, 2, 2, 2, 2, 2, 2, 0, 0},
 {{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1},
  {0, 0, 0, 0, 0, 0, 0, 1, 0, 0, 0, 1, 0, 1, 1, 0},
  {0, 0, 0, 1, 0, 1, 1, 0, 0, 1, 1, 0, 1, 0, 0, 0},
  {0, 1, 1, 0, 1, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0},
  {1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, -1, 0, 0, 0, 0, 0, 0, 1, 0},
  {0, 0, 0, 0, 0, 0, 0, -1, 0, 0, 0, 0, 0, 1, 0, 0},
  {0, 0, 0, -1, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, 0, -1, 0, 0, 0, 1, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, -1, 0, 0, 0, 0, 1, 0, 0, 0, 0, 0},
  {0, 0, 0, 0, 0, 0, -1, 0, 0, 1, 0, 0, 0, 0, 0, 0},
  {0, -1, 0, 0, 0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0},
  {0, -1, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, -1, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0},
  {0, 0, 0, 1, 0, 0, -1, 0, 0, -1, 0, 0, 1, 0, 0, 0},
  {0, 0, 0, 0, 0, 1, -1, 0, 0, -1, 1, 0, 0, 0, 0, 0}}}
```

```
χ1 = eq1[[2, 1]]; χ2 = eq1[[2, 2]]; χ3 = eq1[[2, 3]]; χ4 = eq1[[2, 4]];
χ5 = eq1[[2, 5]]; χ6 = eq1[[2, 6]]; χ7 = eq1[[2, 7]]; χ8 = eq1[[2, 8]];
χ9 = eq1[[2, 9]]; χ10 = eq1[[2, 10]]; χ11 = eq1[[2, 11]]; χ12 = eq1[[2, 12]];
χ13 = eq1[[2, 13]]; χ14 = eq1[[2, 14]]; χ15 = eq1[[2, 15]];
χ16 = eq1[[2, 16]];
```

```
eq2 = Orthogonalize[{χ1, χ2, χ3, χ4, χ5, χ6, χ7, χ8, χ9, χ10, χ11,
   χ12, χ13, χ14, χ15, χ16 }]
```

$$\Big\{\{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1\},$$

$$\left\{0, 0, 0, 0, 0, 0, 0, \frac{1}{2}, 0, 0, 0, \frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2}, 0\right\},$$

$$\left\{0, 0, 0, \frac{1}{\sqrt{6}}, 0, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, 0, 0, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, 0, \frac{1}{\sqrt{6}}, 0, 0, 0\right\},$$

$$\left\{0, \frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}, 0, 0, 0, \frac{1}{2}, 0, 0, 0, 0, 0, 0, 0\right\},$$

$$\{1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\},$$

$$\left\{0, 0, 0, 0, 0, 0, 0, -\frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0, \frac{1}{\sqrt{2}}, 0\right\},$$

$$\left\{0, 0, 0, 0, 0, 0, 0, -\frac{1}{\sqrt{6}}, 0, 0, 0, 0, 0, \sqrt{\frac{2}{3}}, -\frac{1}{\sqrt{6}}, 0\right\},$$

$$\left\{0, 0, 0, -\frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0, 0, 0, \frac{1}{\sqrt{2}}, 0, 0, 0\right\},$$

$$\left\{0, 0, 0, 0, 0, 0, 0, -\frac{1}{2\sqrt{3}}, 0, 0, 0, \frac{\sqrt{3}}{2}, 0, -\frac{1}{2\sqrt{3}}, -\frac{1}{2\sqrt{3}}, 0\right\},$$

$$\left\{0, 0, 0, 0, 0, -\frac{1}{\sqrt{2}}, 0, 0, 0, 0, \frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0\right\},$$

$$\left\{0, 0, 0, 0, 0, 0, -\frac{1}{\sqrt{2}}, 0, 0, \frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0\right\},$$

$$\left\{0, -\frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0, \frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0, 0\right\},$$

$$\left\{0, -\frac{1}{\sqrt{6}}, 0, 0, \sqrt{\frac{2}{3}}, 0, 0, 0, -\frac{1}{\sqrt{6}}, 0, 0, 0, 0, 0, 0, 0\right\},$$

$$\left\{0, -\frac{1}{2\sqrt{3}}, \frac{\sqrt{3}}{2}, 0, -\frac{1}{2\sqrt{3}}, 0, 0, 0, -\frac{1}{2\sqrt{3}}, 0, 0, 0, 0, 0, 0, 0\right\},$$

$$\left\{0, 0, 0, \frac{1}{2}, 0, 0, -\frac{1}{2}, 0, 0, -\frac{1}{2}, 0, 0, \frac{1}{2}, 0, 0, 0\right\},$$

$$\left\{0, 0, 0, -\frac{1}{2\sqrt{3}}, 0, \frac{1}{\sqrt{3}}, -\frac{1}{2\sqrt{3}}, 0, 0, -\frac{1}{2\sqrt{3}}, \frac{1}{\sqrt{3}}, 0, -\frac{1}{2\sqrt{3}}, 0, 0, 0\right\}\Big\}$$

```
Φ1 = eq2[[4]]; Φ2 = eq2[[3]]; Φ3 = eq2[[2]]; Φ4 = eq2[[1]]; Φ5 = eq2[[5]];
Φ6 = eq2[[6]]; Φ7 = eq2[[7]]; Φ8 = eq2[[8]]; Φ9 = eq2[[9]]; Φ10 = eq2[[10]];
Φ11 = eq2[[11]]; Φ12 = eq2[[12]]; Φ13 = eq2[[13]]; Φ14 = eq2[[14]];
Φ15 = eq2[[15]];
Φ16 = eq2[[16]];

Sz =
  1/2 (KroneckerProduct[σz, I2, I2, I2] + KroneckerProduct[I2, σz, I2, I2] +
     KroneckerProduct[I2, I2, σz, I2] + KroneckerProduct[I2, I2, I2, σz]);

Sz // MatrixForm
```

$$\begin{pmatrix}
2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2
\end{pmatrix}$$

ST1.Φ1 – 6 Φ1

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Sz.Φ1 – Φ1

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

ST1.Φ2 – 6 Φ2

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Sz.Φ2

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

ST1.Φ3 – 6 Φ3

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Sz.Φ3 + Φ3

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

```
ST1.Φ4 - 6 Φ4
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
Sz.Φ4 + 2 Φ4
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
ST1.Φ5 - 6 Φ5
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
Sz.Φ5 - 2 Φ5
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
ST1.Φ6 - 2 Φ6
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
Sz.Φ6 + Φ6
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
ST1.Φ7 - 2 Φ7 // Simplify
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
```

```
Sz.Φ7 + Φ7
```

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

```
ST1.Φ8 - 2 Φ8 // Simplify
```

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

```
Sz.Φ8
```

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

```
ST1.Φ9 - 2 Φ9 // Simplify
```

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

```
Sz.Φ9 + Φ9
```

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

```
ST1.Φ10 - 2 Φ10 // Simplify
```

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

```
Sz.Φ10
```

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

```
ST1.Φ11 - 2 Φ11 // Simplify
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Sz.Φ11
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

ST1.Φ12 - 2 Φ12 // Simplify
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Sz.Φ12 - Φ12
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

ST1.Φ13 - 2 Φ13 // Simplify
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Sz.Φ13 - Φ13
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

ST1.Φ14 - 2 Φ14 // Simplify
{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}
```

Sz.Φ14 – Φ14

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

ST1.Φ15 // Simplify

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Sz.Φ15

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

ST1.Φ16 // Simplify

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Sz.Φ16

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

{Φ4.Φ5, Φ5.Φ6, Φ6.Φ7, Φ7.Φ8}

{0, 0, 0, 0}

Φ1

$$\left\{0, \frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}, 0, 0, 0, \frac{1}{2}, 0, 0, 0, 0, 0, 0, 0\right\}$$

Φ2

$$\left\{0, 0, 0, \frac{1}{\sqrt{6}}, 0, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, 0, 0, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, 0, \frac{1}{\sqrt{6}}, 0, 0, 0\right\}$$

Φ3

$$\left\{0, 0, 0, 0, 0, 0, 0, \frac{1}{2}, 0, 0, 0, \frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2}, 0\right\}$$

Φ4

{0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1}

Φ5

{1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}

Φ6

$$\left\{0, 0, 0, 0, 0, 0, 0, -\frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0, \frac{1}{\sqrt{2}}, 0\right\}$$

Φ7

$$\left\{0, 0, 0, 0, 0, 0, 0, -\frac{1}{\sqrt{6}}, 0, 0, 0, 0, 0, \sqrt{\frac{2}{3}}, -\frac{1}{\sqrt{6}}, 0\right\}$$

Φ8

$$\left\{0, 0, 0, -\frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0, 0, 0, \frac{1}{\sqrt{2}}, 0, 0, 0\right\}$$

Φ9

$$\left\{0, 0, 0, 0, 0, 0, 0, -\frac{1}{2\sqrt{3}}, 0, 0, 0, \frac{\sqrt{3}}{2}, 0, -\frac{1}{2\sqrt{3}}, -\frac{1}{2\sqrt{3}}, 0\right\}$$

Φ10

$$\left\{0, 0, 0, 0, 0, -\frac{1}{\sqrt{2}}, 0, 0, 0, 0, \frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0\right\}$$

Φ11

$$\left\{0, 0, 0, 0, 0, 0, -\frac{1}{\sqrt{2}}, 0, 0, \frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0\right\}$$

Φ12

$$\left\{0, -\frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0, \frac{1}{\sqrt{2}}, 0, 0, 0, 0, 0, 0, 0\right\}$$

Φ13

$$\left\{0, -\frac{1}{\sqrt{6}}, 0, 0, \sqrt{\frac{2}{3}}, 0, 0, 0, -\frac{1}{\sqrt{6}}, 0, 0, 0, 0, 0, 0, 0\right\}$$

Φ14

$$\left\{0, -\frac{1}{2\sqrt{3}}, \frac{\sqrt{3}}{2}, 0, -\frac{1}{2\sqrt{3}}, 0, 0, 0, -\frac{1}{2\sqrt{3}}, 0, 0, 0, 0, 0, 0, 0\right\}$$

Φ15

$$\left\{0, 0, 0, \frac{1}{2}, 0, 0, -\frac{1}{2}, 0, 0, -\frac{1}{2}, 0, 0, \frac{1}{2}, 0, 0, 0\right\}$$

Φ16

$$\left\{0, 0, 0, -\frac{1}{2\sqrt{3}}, 0, \frac{1}{\sqrt{3}}, -\frac{1}{2\sqrt{3}}, 0, 0, -\frac{1}{2\sqrt{3}}, \frac{1}{\sqrt{3}}, 0, -\frac{1}{2\sqrt{3}}, 0, 0, 0\right\}$$

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APPENDIX
Mathematica

1. Clebsch-Gordan coefficient

ClebschGordan

ClebschGordan[{j_1, m_1}, {j_2, m_2}, {j, m}]
gives the Clebsch-Gordan coefficient for the decomposition of $|j, m\rangle$ in terms of $|j_1, m_1\rangle|j_2, m_2\rangle$.

Details

- The Clebsch-Gordan coefficients vanish except when $m = m_1 + m_2$ and the j_i satisfy a triangle inequality.
- The parameters of ClebschGordan can be integers, half-integers, or symbolic expressions.
- *Mathematica* uses the standard conventions of Edmonds for the phase of the Clebsch-Gordan coefficients.

2. KroneckerProduct

KroneckerProduct

KroneckerProduct[m_1, m_2, …]
constructs the Kronecker product of the arrays m_i.

Details

- KroneckerProduct works on vectors, matrices, or in general, full arrays of any depth.
- For matrices, KroneckerProduct gives the matrix direct product.
- KroneckerProduct can be used on SparseArray objects, returning a SparseArray object when possible. »

3. Eigensystem

Eigensystem

`Eigensystem[m]`
gives a list {*values*, *vectors*} of the eigenvalues and eigenvectors of the square matrix *m*.

`Eigensystem[{m, a}]`
gives the generalized eigenvalues and eigenvectors of *m* with respect to *a*.

`Eigensystem[m, k]`
gives the eigenvalues and eigenvectors for the first *k* eigenvalues of *m*.

`Eigensystem[{m, a}, k]`
gives the first *k* generalized eigenvalues and eigenvectors.

Details and Options

- `Eigensystem` finds numerical eigenvalues and eigenvectors if *m* contains approximate real or complex numbers.
- For approximate numerical matrices *m*, the eigenvectors are normalized.
- All the non-zero eigenvectors given are independent. If the number of eigenvectors is equal to the number of non-zero eigenvalues, then corresponding eigenvalues and eigenvectors are given in corresponding positions in their respective lists.
- If there are more eigenvalues than independent eigenvectors, then each extra eigenvalue is paired with a vector of zeros. »

100%