Exchange interaction, Zeeman energy for spin 1/2
the use of Kronecker product and eigensystem of Mathematica

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
(Date October 23, 2013)

1. Exchange interaction

We solve the eigenvalue problem for the exchange interaction between two spins (electron and proton) using the KroneckerProduct in Mathematica. Note that both electron and proton are spin 1/2 particles.

$$\left|+z\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \left|-z\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

$$\left|\chi_1\right\rangle = \left|+z\right\rangle_1 \otimes \left|+z\right\rangle_2 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \qquad \left|\chi_2\right\rangle = \left|+z\right\rangle_1 \otimes \left|-z\right\rangle_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix},$$

$$\left|\chi_3\right\rangle = \left|-z\right\rangle_1 \otimes \left|+z\right\rangle_2 = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \qquad \left|\chi_4\right\rangle = \left|-z\right\rangle_1 \otimes \left|-z\right\rangle_2 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix},$$

The exchange interaction between the electron and the proton is given by

$$\hat{J} = \hat{\sigma}_{1x} \otimes \hat{\sigma}_{2x} + \hat{\sigma}_{1y} \otimes \hat{\sigma}_{2y} + \hat{\sigma}_{1z} \otimes \hat{\sigma}_{2z} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

which is 4 x 4 matrix. We solve the eigenvalue problem, by using Mathematica (KroneckerProduct and Eigensystem).

Eigensystem[$\hat{J}$]:

Eigenvalues and eigenkets

(i) Triplet state (symmetric state)

E_1=1 $$|\psi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = |\chi_1\rangle$$

E_2=1, $$|\psi_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}(|\chi_2\rangle + |\chi_3\rangle)$$

E_3=1 $$|\psi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = |\chi_4\rangle$$

(ii) Singlet state (anti-symmetric state):

E_4=-3 $$|\psi_4\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}(|\chi_2\rangle - |\chi_3\rangle)$$

The unitary operator is defined by

$$|\psi_i\rangle = \hat{U}|\chi_i\rangle,$$

and is expressed by

$$\hat{U} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ 0 & 0 & 1 & 0 \end{pmatrix}, \qquad \hat{U}^+ = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix}$$

We also have

$$\hat{U}^{+}\hat{J}\hat{U}=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&-3\end{pmatrix}\qquad \text{(diagonal matrix)}$$

((**Mathematica**))

```
Clear["Global`*"];
exp_* := exp /. {Complex[re_, im_] :> Complex[re, -im]}; ψ1 = (1
                                                               0); ψ1 = (1
                                                                         0);
ψ1 = (1
      0); ψ2 = (0
                1); σx = (0 1
                          1 0); σy = (0 -ⅈ
                                      ⅈ  0); σz = (1  0
                                                   0 -1);
I2 = IdentityMatrix[2];

ϕ1 = KroneckerProduct[ψ1, ψ1]; ϕ2 = KroneckerProduct[ψ1, ψ2];
ϕ3 = KroneckerProduct[ψ2, ψ1];
ϕ4 = KroneckerProduct[ψ2, ψ2];

J1 = (KroneckerProduct[σx, σx] + KroneckerProduct[σy, σy]
    + KroneckerProduct[σz, σz]);

J1 // MatrixForm
```

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

```
eq1 = Eigensystem[J1]
```

{{-3, 1, 1, 1}, {{0, -1, 1, 0}, {0, 0, 0, 1}, {0, 1, 1, 0}, {1, 0, 0, 0}}}

```
χ1 = Normalize[eq1[[2, 4]]]
```

{1, 0, 0, 0}

```
χ2 = Normalize[eq1[[2, 3]]]
```

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

```
χ3 = Normalize[eq1[[2, 2]]]
```

{0, 0, 0, 1}

```
χ4 = -Normalize[eq1[[2, 1]]]
```

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

```
UT = {χ1, χ2, χ3, χ4}; U = Transpose[UT]; UH = UT*;
```

```
U // MatrixForm
```

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

```
UH // MatrixForm
```

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

```
UH.U // Simplify
```

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

```
eq2 = UH.J1.U // FullSimplify; eq2 // MatrixForm
```

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

2. Dirac spin exchange operator

$$\hat{J}|\psi_1\rangle = |\psi_1\rangle, \qquad \hat{J}|\chi_1\rangle = |\chi_1\rangle$$

$$\hat{J}|\psi_3\rangle = |\psi_3\rangle, \qquad \hat{J}|\chi_4\rangle = |\chi_4\rangle$$

$$\hat{J}|\psi_2\rangle = |\psi_2\rangle, \qquad \hat{J}(|\chi_2\rangle + |\chi_3\rangle) = |\chi_2\rangle + |\chi_3\rangle$$

$$\hat{J}|\psi_4\rangle = -3|\psi_4\rangle, \qquad \hat{J}(|\chi_2\rangle - |\chi_3\rangle) = -3|\chi_2\rangle + 3|\chi_3\rangle)$$

Then we have

$$\left(\frac{\hat{J}+\hat{1}}{2}\right)|\chi_1\rangle = |\chi_1\rangle, \qquad \left(\frac{\hat{J}+\hat{1}}{2}\right)|\chi_4\rangle = |\chi_4\rangle$$

$$\left(\frac{\hat{J}+\hat{1}}{2}\right)|\chi_3\rangle = |\chi_2\rangle, \qquad \left(\frac{\hat{J}+\hat{1}}{2}\right)|\chi_2\rangle = |\chi_3\rangle$$

In other words, we can define the Dirac spin exchange operator

$$\hat{P}_{12} = \frac{1}{2}(\hat{1}+\hat{J}) = \frac{1}{2}(\hat{1}+\hat{\boldsymbol{\sigma}}_1\cdot\hat{\boldsymbol{\sigma}}_2)$$

where for example,

$$\hat{P}_{12}|+z\rangle_1 \otimes |-z\rangle_2 = |+z\rangle_1 \otimes |-z\rangle_2$$

3. Total spin angular momentum

The total spin angular momentum:

$$\hat{\boldsymbol{S}} = \hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2 = \frac{\hbar}{2}(\hat{\boldsymbol{\sigma}}_1 + \hat{\boldsymbol{\sigma}}_2)$$

Then we have

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

and

$$\hat{S}_z = \frac{\hbar}{2}(\hat{\sigma}_{1z} + \hat{\sigma}_{2z}) = \frac{\hbar}{2}(\hat{\sigma}_{1z}\otimes\hat{1}_2 + \hat{1}_1\otimes\hat{\sigma}_{2z})$$

We get

$$\hat{\boldsymbol{S}}^2 = \hbar^2\begin{pmatrix}2 & 0 & 0 & 0\\ 0 & 1 & 1 & 0\\ 0 & 1 & 1 & 0\\ 0 & 0 & 0 & 2\end{pmatrix}, \qquad \hat{S}_z = \hbar\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & -1\end{pmatrix}$$

and the commutation relation

$$[\hat{\boldsymbol{S}}^2, \hat{S}_z] = 0$$

In summary

$$|\psi_1\rangle = |l = 1, m = 1\rangle, \qquad |\psi_2\rangle = |l = 1, m = 0\rangle, \qquad |\psi_3\rangle = |l = 1, m = -1\rangle$$

$$|\psi_4\rangle = |l = 0, m = 0\rangle$$

((**Mathematica-2**))

Simultaneous eigenkets of $\hat{\boldsymbol{S}}^2$ and $\hat{S}_z$. The Mathematica program-2 is the sequence of the Mmathematica program-1.

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

ST = 3ħ^2/2 KroneckerProduct[I2, I2] + ħ^2/2 J1;

Sz // MatrixForm
```

$$\begin{pmatrix} \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar \end{pmatrix}$$

```
ST // MatrixForm
```

$$\begin{pmatrix} 2\hbar^2 & 0 & 0 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & 0 & 0 & 2\hbar^2 \end{pmatrix}$$

```
Sz.ST – ST.Sz // Simplify
```

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

```
Sz.χ1 – ℏ χ1
```

{0, 0, 0, 0}

```
Sz.χ2
```

{0, 0, 0, 0}

```
Sz.χ3 + ℏ χ3
```

{0, 0, 0, 0}

```
Sz.χ4
```

{0, 0, 0, 0}

```
ST.χ1 – 2 ℏ^2 χ1
```

{0, 0, 0, 0}

```
ST.χ2 – 2 ℏ^2 χ2
```

{0, 0, 0, 0}

```
ST.χ3 – 2 ℏ^2 χ3
```

{0, 0, 0, 0}

```
ST.χ4
```

{0, 0, 0, 0}

4. Zeeman energy

We consider the Hamiltonian consists of the exchange interaction and the Zeeman energy is given by

$$\begin{aligned}\hat{H} &= J\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2 - \mu_1 B\hat{\sigma}_{1z} - \mu_1 B\hat{\sigma}_{2z} \\ &= J(\hat{\sigma}_{1x} \otimes \hat{\sigma}_{2x} + \hat{\sigma}_{1y} \otimes \hat{\sigma}_{2y} + \hat{\sigma}_{1z} \otimes \hat{\sigma}_{2z}) - \mu_1 B(\hat{\sigma}_{1z} \otimes \hat{1}_2) - \mu_2 B(\hat{1}_1 \otimes \hat{\sigma}_{2z})\end{aligned}$$

This Hamiltonian can be described by the 4x4 matrix given by

$$\hat{H} = \begin{pmatrix} J-\mu_1 B-\mu_2 B & 0 & 0 & 0 \\ 0 & -J-\mu_1 B+\mu_2 B & 2J & 0 \\ 0 & 2J & -J+\mu_1 B-\mu_2 B & 0 \\ 0 & 0 & 0 & J+\mu_1 B+\mu_2 B \end{pmatrix}$$

So we can solve the eigenvalue problems. There are four eigenvalues and four eigenkets.

(i) Energy eigenvalue Eigenket

$J-(\mu_1+\mu_2)B$ $\qquad$ $\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$

(ii) Energy eigenvalue Eigenket

$-J+\sqrt{4J^2+B^2(\mu_1-\mu_2)^2}$ $\qquad$ $\begin{pmatrix} 0 \\ [\sqrt{4J^2+B^2(\mu_1-\mu_2)^2}-(\mu_1-\mu_2)B]/2J \\ 1 \\ 0 \end{pmatrix}$

which corresponds to the state $\frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix}$ $\qquad$ $(=|j=1, m=0\rangle)$

(iii) Energy eigenvalue Eigenket

$J+(\mu_1+\mu_2)B$ $\qquad$ $\begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$

(iv) Energy eigenvalue Eigenket

$$-J-\sqrt{4J^2+B^2(\mu_1-\mu_2)^2} \qquad \begin{pmatrix} 0 \\ [\sqrt{4J^2+B^2(\mu_1-\mu_2)^2}+(\mu_1-\mu_2)B]/2J \\ -1 \\ 0 \end{pmatrix}$$

which corresponds to the state $\frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix}$ $\qquad (=|j=0,m=0\rangle)$

Note that the eigenkets are not normalized.

((Mthaemtica))

```
Clear["Global`*"];
exp_* := exp /. {Complex[re_, im_] :→ Complex[re, -im]}; ψ1 = (1
                                                              0); ψ1 = (1
                                                                        0);
ψ1 = (1
      0); ψ2 = (0
                1); σx = (0 1
                          1 0); σy = (0 -ⅈ
                                      ⅈ  0); σz = (1  0
                                                   0 -1);
I2 = IdentityMatrix[2];

ϕ1 = KroneckerProduct[ψ1, ψ1]; ϕ2 = KroneckerProduct[ψ1, ψ2];
ϕ3 = KroneckerProduct[ψ2, ψ1];
ϕ4 = KroneckerProduct[ψ2, ψ2];

K1 = J (KroneckerProduct[σx, σx] + KroneckerProduct[σy, σy]
    + KroneckerProduct[σz, σz]);
K2 = -μ1 B KroneckerProduct[σz, I2] - μ2 B KroneckerProduct[I2, σz];
H1 = K1 + K2; H1 // MatrixForm
```

$$\begin{pmatrix} J-B\mu1-B\mu2 & 0 & 0 & 0 \\ 0 & -J-B\mu1+B\mu2 & 2J & 0 \\ 0 & 2J & -J+B\mu1-B\mu2 & 0 \\ 0 & 0 & 0 & J+B\mu1+B\mu2 \end{pmatrix}$$

```
eq1 = Eigensystem[H1] // Simplify
```

$$\Big\{\Big\{J-B(\mu1+\mu2),\ J+B(\mu1+\mu2),\ -J-\sqrt{4J^2+B^2(\mu1-\mu2)^2},\ -J+\sqrt{4J^2+B^2(\mu1-\mu2)^2}\Big\},$$
$$\Big\{\{1,0,0,0\},\{0,0,0,1\},\Big\{0,\frac{-\sqrt{4J^2+B^2(\mu1-\mu2)^2}+B(-\mu1+\mu2)}{2J},1,0\Big\},$$
$$\Big\{0,\frac{\sqrt{4J^2+B^2(\mu1-\mu2)^2}+B(-\mu1+\mu2)}{2J},1,0\Big\}\Big\}\Big\}$$

REFERENCES

John S. Townsend , *A Modern Approach to Quantum Mechanics*, second edition (University Science Books, 2012).