自旋轨道耦合

自旋轨道耦合(SOC)作用的一般表达式:

$$H_{SO}=\frac{\hbar}{4m_0^2c^2}(\nabla V_0\times\vec{p})\cdot\vec{\sigma}$$

式中$\hbar, m_0, c$和$\vec{p}$分别是约化普朗克常数、电子质量、光速和动量算符; V_0是原子核的库仑势; $\vec{\sigma}$是泡利矩阵矢量。简单起见, 仅考虑在位项, 有:

$$H_{SO}=\lambda(\vec{r}\times\vec{p})=\lambda\hat{L}\cdot\hat{S}=\frac{\lambda}{2}\hat{L}\cdot\hat{\sigma}$$

式中λ为一与原子种类有关的系数。

为计算$\hat{L}\cdot\hat{S}$, 写出上升、下降算符:

$$\begin{cases}\hat{L}_+=\hat{L}_x+i\hat{L}_y\\ \hat{L}_-=\hat{L}_x-i\hat{L}_y\\ \hat{S}_+=\hat{S}_x+i\hat{S}_y\\ \hat{S}_-=\hat{S}_x-i\hat{S}_y\end{cases}$$

有如下变换关系:

$$\begin{cases}\hat{L}_x=\dfrac{\hat{L}_++\hat{L}_-}{2}\\ \hat{L}_y=\dfrac{\hat{L}_+-\hat{L}_-}{2i}\\ \hat{S}_x=\dfrac{\hat{S}_++\hat{S}_-}{2}\\ \hat{S}_y=\dfrac{\hat{S}_+-\hat{S}_-}{2i}\end{cases}$$

代入$\hat{L}\cdot\hat{S}$可得:

$$\begin{aligned}\hat{L}\cdot\hat{S}&=\hat{L}_x\hat{S}_x+\hat{L}_y\hat{S}_y+\hat{L}_z\hat{S}_z\\&=\frac{\hat{L}_++\hat{L}_-}{2}\frac{\hat{S}_++\hat{S}_-}{2}+\frac{\hat{L}_+-\hat{L}_-}{2i}\frac{\hat{S}_+-\hat{S}_-}{2i}+\hat{L}_z\hat{S}_z\\&=\frac{1}{2}\left(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+\right)+\hat{L}_z\hat{S}_z\end{aligned}$$

下面求取算符$\hat{L}\cdot\hat{S}$在原子轨道基组$\{s, p_{x,y,z}, d_{xy,yz,xz,x^2-y^2,z^2}\}$下的矩阵元。

设: $Y_l^m=|l,m\rangle$,

s	$\|0,0\rangle$	$\langle 0,0\|$
p_x	$\frac{1}{\sqrt{2}}(-\|1,1\rangle+\|1,-1\rangle)$	$\frac{1}{\sqrt{2}}(-\langle 1,1\|+\langle 1,-1\|)$
p_y	$\frac{i}{\sqrt{2}}(\|1,1\rangle+\|1,-1\rangle)$	$\frac{-i}{\sqrt{2}}(\langle 1,1\|+\langle 1,-1\|)$
p_z	$\|1,0\rangle$	$\langle 1,0\|$
d_{xy}	$\frac{i}{\sqrt{2}}(\|2,-2\rangle-\|2,2\rangle)$	$\frac{-i}{\sqrt{2}}(\langle 2,-2\|-\langle 2,2\|)$
d_{yz}	$\frac{i}{\sqrt{2}}(\|2,-1\rangle+\|2,1\rangle)$	$\frac{-i}{\sqrt{2}}(\langle 2,-1\|+\langle 2,1\|)$
d_{xz}	$\frac{1}{\sqrt{2}}(\|2,-1\rangle-\|2,1\rangle)$	$\frac{1}{\sqrt{2}}(\langle 2,-1\|-\langle 2,1\|)$
$d_{x^2-y^2}$	$\frac{1}{\sqrt{2}}(\|2,-2\rangle+\|2,2\rangle)$	$\frac{1}{\sqrt{2}}(\langle 2,-2\|+\langle 2,2\|)$
d_{z^2}	$\|2,0\rangle$	$\langle 2,0\|$

对轨道角动量算符有如下关系:

$$\begin{cases}\hat{L}_+|l,m\rangle=\sqrt{l(l+1)-m(m+1)}|l,m+1\rangle\\ \hat{L}_-|l,m\rangle=\sqrt{l(l+1)-m(m-1)}|l,m-1\rangle\\ \hat{L}_z|l,m\rangle=m|l,m\rangle\end{cases}$$

计算系数表格:

$\|l,m\rangle$	$\hat{L}_+$	$\hat{L}_-$	$\hat{L}_z$
$\|0,0\rangle$	0	0	0
$\|1,1\rangle$	0	$\sqrt{2}\|1,0\rangle$	$\|1,1\rangle$
$\|1,0\rangle$	$\sqrt{2}\|1,1\rangle$	$\sqrt{2}\|1,-1\rangle$	0
$\|1,-1\rangle$	$\sqrt{2}\|1,0\rangle$	0	$-\|1,-1\rangle$
$\|2,2\rangle$	0	$2\|2,1\rangle$	$2\|2,2\rangle$
$\|2,1\rangle$	$2\|2,2\rangle$	$\sqrt{6}\|2,0\rangle$	$\|2,1\rangle$
$\|2,0\rangle$	$\sqrt{6}\|2,1\rangle$	$\sqrt{6}\|2,-1\rangle$	0
$\|2,-1\rangle$	$\sqrt{6}\|2,0\rangle$	$2\|2,-2\rangle$	$-\|2,-1\rangle$
$\|2,-2\rangle$	$2\|2,-1\rangle$	0	$-2\|2,-2\rangle$

矩阵元表格:

$\langle 0\|\hat{L}_{+,-,z}\|0\rangle$	$\|0,0\rangle$
$\langle 0,0\|$	0

$\langle 1\|\hat{L}_+\|1\rangle$	$\|1,1\rangle$	$\|1,0\rangle$	$\|1,-1\rangle$
$\langle 1,1\|$	0	$\sqrt{2}$	0
$\langle 1,0\|$	0	0	$\sqrt{2}$
$\langle 1,-1\|$	0	0	0

$\langle 1\|\hat{L}_-\|1\rangle$	$\|1,1\rangle$	$\|1,0\rangle$	$\|1,-1\rangle$
$\langle 1,1\|$	0	0	0
$\langle 1,0\|$	$\sqrt{2}$	0	0
$\langle 1,-1\|$	0	$\sqrt{2}$	0

$\langle 2\|\hat{L}_+\|2\rangle$	$\|2,2\rangle$	$\|2,1\rangle$	$\|2,0\rangle$	$\|2,-1\rangle$	$\|2,-2\rangle$
$\langle 2,2\|$	0	2	0	0	0
$\langle 2,1\|$	0	0	$\sqrt{6}$	0	0
$\langle 2,0\|$	0	0	0	$\sqrt{6}$	0
$\langle 2,-1\|$	0	0	0	0	2
$\langle 2,-2\|$	0	0	0	0	0

$\langle 2\|\hat{L}_-\|2\rangle$	$\|2,2\rangle$	$\|2,1\rangle$	$\|2,0\rangle$	$\|2,-1\rangle$	$\|2,-2\rangle$
$\langle 2,2\|$	0	0	0	0	0
$\langle 2,1\|$	2	0	0	0	0
$\langle 2,0\|$	0	$\sqrt{6}$	0	0	0
$\langle 2,-1\|$	0	0	$\sqrt{6}$	0	0
$\langle 2,-2\|$	0	0	0	2	0

$\langle 1\|\hat{L}_z\|1\rangle$	$\|1,1\rangle$	$\|1,0\rangle$	$\|1,-1\rangle$
$\langle 1,1\|$	1	0	0
$\langle 1,0\|$	0	0	0
$\langle 1,-1\|$	0	0	-1

$\langle 2\|\hat{L}_z\|2\rangle$	$\|2,2\rangle$	$\|2,1\rangle$	$\|2,0\rangle$	$\|2,-1\rangle$	$\|2,-2\rangle$
$\langle 2,2\|$	2	0	0	0	0
$\langle 2,1\|$	0	1	0	0	0
$\langle 2,0\|$	0	0	0	0	0
$\langle 2,-1\|$	0	0	0	-1	0
$\langle 2,-2\|$	0	0	0	0	-2

对自旋角动量算符有如下关系（令$\hbar=1$）:

$$\begin{cases}\hat{S}_x|\uparrow\rangle=\frac{1}{2}\hat{\sigma}_x|\uparrow\rangle=\frac{1}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\frac{1}{2}\begin{pmatrix}0\\1\end{pmatrix}=\frac{1}{2}|\downarrow\rangle\\ \hat{S}_y|\uparrow\rangle=\frac{1}{2}\hat{\sigma}_y|\uparrow\rangle=\frac{1}{2}\begin{pmatrix}0&-i\\i&0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\frac{i}{2}\begin{pmatrix}0\\1\end{pmatrix}=\frac{i}{2}|\downarrow\rangle\\ \hat{S}_z|\uparrow\rangle=\frac{1}{2}\hat{\sigma}_z|\uparrow\rangle=\frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\frac{1}{2}\begin{pmatrix}1\\0\end{pmatrix}=\frac{1}{2}|\uparrow\rangle\\ \hat{S}_x|\downarrow\rangle=\frac{1}{2}\hat{\sigma}_x|\downarrow\rangle=\frac{1}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}=\frac{1}{2}\begin{pmatrix}1\\0\end{pmatrix}=\frac{1}{2}|\uparrow\rangle\\ \hat{S}_y|\downarrow\rangle=\frac{1}{2}\hat{\sigma}_y|\downarrow\rangle=\frac{1}{2}\begin{pmatrix}0&-i\\i&0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}=\frac{-i}{2}\begin{pmatrix}1\\0\end{pmatrix}=\frac{-i}{2}|\uparrow\rangle\\ \hat{S}_z|\downarrow\rangle=\frac{1}{2}\hat{\sigma}_z|\downarrow\rangle=\frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}=\frac{-1}{2}\begin{pmatrix}0\\1\end{pmatrix}=\frac{-1}{2}|\downarrow\rangle\end{cases}$$

可得:

$$
\begin{cases}
\hat{S}_+|\uparrow\rangle = (\hat{S}_x + i\hat{S}_y)|\uparrow\rangle = \frac{1}{2}|\downarrow\rangle + i\frac{i}{2}|\downarrow\rangle = 0 \\
\hat{S}_-|\uparrow\rangle = (\hat{S}_x - i\hat{S}_y)|\uparrow\rangle = \frac{1}{2}|\downarrow\rangle - i\frac{i}{2}|\downarrow\rangle = |\downarrow\rangle \\
\hat{S}_z|\uparrow\rangle = \frac{1}{2}|\uparrow\rangle \\
\hat{S}_+|\downarrow\rangle = (\hat{S}_x + i\hat{S}_y)|\downarrow\rangle = \frac{1}{2}|\uparrow\rangle + i\frac{-i}{2}|\uparrow\rangle = |\uparrow\rangle \\
\hat{S}_-|\downarrow\rangle = (\hat{S}_x - i\hat{S}_y)|\downarrow\rangle = \frac{1}{2}|\uparrow\rangle - i\frac{-i}{2}|\uparrow\rangle = 0 \\
\hat{S}_z|\downarrow\rangle = \frac{-1}{2}|\downarrow\rangle
\end{cases}
$$

矩阵元表格:

$S =$	$\hat{S}_+$	$\hat{S}_-$	$\hat{S}_z$
$\langle\uparrow\|S\|\uparrow\rangle$	0	0	$\frac{1}{2}$
$\langle\uparrow\|S\|\downarrow\rangle$	1	0	0
$\langle\downarrow\|S\|\uparrow\rangle$	0	1	0
$\langle\downarrow\|S\|\downarrow\rangle$	0	0	$-\frac{1}{2}$

由上述结果可以求解$\hat{L}\cdot\hat{S}$矩阵元:

规律如下:

1. $l = 0$则矩阵元必为零，即 s 轨道不贡献 SOC;
2. l不同则矩阵元必为零，即无需考虑 p-d 等耦合;
3. 自旋相同则$\hat{S}_\pm$项贡献为零，自旋相反则$\hat{S}_z$项贡献为零;
4. m相同则矩阵元必为零，即对角元全为零;

$\langle s\vert\hat{L}\cdot\hat{S}\vert s\rangle$	$\vert s\rangle$
$\langle s\vert$	0

$\langle p^{\uparrow}\vert\hat{L}\cdot\hat{S}\vert p^{\uparrow}\rangle$	$\vert p_x^{\uparrow}\rangle$	$\vert p_y^{\uparrow}\rangle$	$\vert p_z^{\uparrow}\rangle$
$\langle p_x^{\uparrow}\vert$	0	$-i/2$	0
$\langle p_y^{\uparrow}\vert$	$i/2$	0	0
$\langle p_z^{\uparrow}\vert$	0	0	0

$\langle p^{\downarrow}\vert\hat{L}\cdot\hat{S}\vert p^{\downarrow}\rangle$	$\vert p_x^{\downarrow}\rangle$	$\vert p_y^{\downarrow}\rangle$	$\vert p_z^{\downarrow}\rangle$
$\langle p_x^{\downarrow}\vert$	0	$i/2$	0
$\langle p_y^{\downarrow}\vert$	$-i/2$	0	0
$\langle p_z^{\downarrow}\vert$	0	0	0

$\langle p^{\uparrow}\vert\hat{L}\cdot\hat{S}\vert p^{\downarrow}\rangle$	$\vert p_x^{\downarrow}\rangle$	$\vert p_y^{\downarrow}\rangle$	$\vert p_z^{\downarrow}\rangle$
$\langle p_x^{\uparrow}\vert$	0	0	$\frac{1}{2}$
$\langle p_y^{\uparrow}\vert$	0	0	$-\frac{i}{2}$
$\langle p_z^{\uparrow}\vert$	$-\frac{1}{2}$	$\frac{i}{2}$	0

$\langle p^{\downarrow}\vert\hat{L}\cdot\hat{S}\vert p^{\uparrow}\rangle$	$\vert p_x^{\uparrow}\rangle$	$\vert p_y^{\uparrow}\rangle$	$\vert p_z^{\uparrow}\rangle$
$\langle p_x^{\downarrow}\vert$	0	0	$-\frac{1}{2}$
$\langle p_y^{\downarrow}\vert$	0	0	$-\frac{i}{2}$
$\langle p_z^{\downarrow}\vert$	$\frac{1}{2}$	$\frac{i}{2}$	0

$\langle d^{\uparrow}\vert\hat{L}\cdot\hat{S}\vert d^{\uparrow}\rangle$	$\vert d_{xy}^{\uparrow}\rangle$	$\vert d_{yz}^{\uparrow}\rangle$	$\vert d_{xz}^{\uparrow}\rangle$	$\vert d_{x^2}^{\uparrow}\rangle$	$\vert d_{z^2}^{\uparrow}\rangle$
$\langle d_{xy}^{\uparrow}\vert$	0	0	0	$2i$	0
$\langle d_{yz}^{\uparrow}\vert$	0	0	i	0	0
$\langle d_{xz}^{\uparrow}\vert$	0	$-i$	0	0	0
$\langle d_{x^2}^{\uparrow}\vert$	$-2i$	0	0	0	0
$\langle d_{z^2}^{\uparrow}\vert$	0	0	0	0	0

$\langle d^{\downarrow}\vert\hat{L}\cdot\hat{S}\vert d^{\downarrow}\rangle$	$\vert d_{xy}^{\downarrow}\rangle$	$\vert d_{yz}^{\downarrow}\rangle$	$\vert d_{xz}^{\downarrow}\rangle$	$\vert d_{x^2}^{\downarrow}\rangle$	$\vert d_{z^2}^{\downarrow}\rangle$
$\langle d_{xy}^{\downarrow}\vert$	0	0	0	$-2i$	0
$\langle d_{yz}^{\downarrow}\vert$	0	0	$-i$	0	0
$\langle d_{xz}^{\downarrow}\vert$	0	i	0	0	0
$\langle d_{x^2}^{\downarrow}\vert$	$2i$	0	0	0	0
$\langle d_{z^2}^{\downarrow}\vert$	0	0	0	0	0

$\langle d^{\uparrow}\vert\hat{L}\cdot\hat{S}\vert d^{\downarrow}\rangle$	$\vert d_{xy}^{\downarrow}\rangle$	$\vert d_{yz}^{\downarrow}\rangle$	$\vert d_{xz}^{\downarrow}\rangle$	$\vert d_{x^2}^{\downarrow}\rangle$	$\vert d_{z^2}^{\downarrow}\rangle$
$\langle d_{xy}^{\uparrow}\vert$	0	$\frac{1}{2}$	$-\frac{i}{2}$	0	0
$\langle d_{yz}^{\uparrow}\vert$	$-\frac{1}{2}$	0	0	$-\frac{i}{2}$	$-\frac{\sqrt{3}i}{2}$
$\langle d_{xz}^{\uparrow}\vert$	$\frac{i}{2}$	0	0	$-\frac{1}{2}$	$\frac{\sqrt{3}}{2}$
$\langle d_{x^2}^{\uparrow}\vert$	0	$\frac{i}{2}$	$\frac{1}{2}$	0	0
$\langle d_{z^2}^{\uparrow}\vert$	0	$\frac{\sqrt{3}i}{2}$	$-\frac{\sqrt{3}}{2}$	0	0

$\langle d^{\downarrow}\vert\hat{L}\cdot\hat{S}\vert d^{\uparrow}\rangle$	$\vert d_{xy}^{\uparrow}\rangle$	$\vert d_{yz}^{\uparrow}\rangle$	$\vert d_{xz}^{\uparrow}\rangle$	$\vert d_{x^2}^{\uparrow}\rangle$	$\vert d_{z^2}^{\uparrow}\rangle$
$\langle d_{xy}^{\downarrow}\vert$	0	$-\frac{1}{2}$	$-\frac{i}{2}$	0	0
$\langle d_{yz}^{\downarrow}\vert$	$\frac{1}{2}$	0	0	$-\frac{i}{2}$	$-\frac{\sqrt{3}i}{2}$
$\langle d_{xz}^{\downarrow}\vert$	$\frac{i}{2}$	0	0	$\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$
$\langle d_{x^2}^{\downarrow}\vert$	0	$\frac{i}{2}$	$-\frac{1}{2}$	0	0
$\langle d_{z^2}^{\downarrow}\vert$	0	$\frac{\sqrt{3}i}{2}$	$\frac{\sqrt{3}}{2}$	0	0

$$\langle x|LS|y\rangle = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = -i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = -i\sigma_z$$

$$\langle y|LS|x\rangle = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} = i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\sigma_z$$

$$\langle y|LS|z\rangle = \begin{pmatrix} 0 & -\frac{i}{2} \\ -\frac{i}{2} & 0 \end{pmatrix} = -\frac{i}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = -\frac{i}{2}\sigma_x$$

$$\langle z|LS|y\rangle = \begin{pmatrix} 0 & \frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix} = \frac{i}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{i}{2}\sigma_x$$

$$\langle x|LS|z\rangle = \begin{pmatrix} 0 & \frac{1}{2} \\ -\frac{1}{2} & 0 \end{pmatrix} = \frac{i}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{i}{2}\sigma_y$$

$$\langle z|LS|x\rangle = \begin{pmatrix} 0 & -\frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} = \frac{-i}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = -\frac{i}{2}\sigma_y$$