自旋轨道耦合

自旋轨道耦合(SOC)作用的一般表达式:

式中和分别是约化普朗克常数、电子质量、光速和动量算符；是原子核的库仑势；是泡利矩阵矢量。简单起见，仅考虑在位项，有：

式中为一与原子种类有关的系数。

为计算，写出上升、下降算符：

有如下变换关系：

代入可得：

下面求取算符在原子轨道基组下的矩阵元。

设：，

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对轨道角动量算符有如下关系：

计算系数表格：

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矩阵元表格：

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对自旋角动量算符有如下关系（令）：

可得：

矩阵元表格：

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由上述结果可以求解矩阵元：

规律如下：

1. 则矩阵元必为零，即s轨道不贡献SOC；
2. 不同则矩阵元必为零，即无需考虑p-d等耦合；
3. 自旋相同则项贡献为零，自旋相反则项贡献为零；
4. 相同则矩阵元必为零，即对角元全为零；

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