Vector Operators

Several interesting operators are rotational vectors; electric and magnetic dipole moments, angular momentum, $\vec{X}$, $\vec{P}$, etc. There are also some operators of interest that are second rank tensors, the electric quadrupole moment operator being the most important. In these notes we will concentrate on vector operators in the case of a single electron atom, without consideration of electron spin.

The property that makes an operator a three vector is really the way it transforms when the coordinate system is rotated. This in turn depends on the commutation rules of the vector operator with the total angular momentum operator. When spin is included the total angular momentum is denoted by $\vec{J}$, while for the case we are considering here the total angular momentum is the orbital angular momentum, $\vec{L}$. For convenience, we will measure angular momentum in units of $\hbar$, so the angular momentum commutation rules read

$$[L_j, L_k] = i\epsilon_{jkm}L_m,$$

where ϵ_{jkm} is the usual totally antisymmetric symbol, and repeated indices are summed. As an example, we have

$$[L_x, L_y] = iL_z, \quad etc$$

We will use both x, y, z and $1, 2, 3$ to label components of our vector operators.

Now the orbital angular momentum is itself a vector operator. Other vectors have commutation rules with $\vec{L}$ which are similar to the angular momentum commutation rules. For a vector operator $\vec{V}$, the commutation rules with $\vec{L}$ are

$$[L_j, V_k] = i\epsilon_{jkm}V_m. \tag{1}$$

Since the components of the angular momentum are the generators of rotations, if these rules are satisfied, the vector operator $\vec{V}$ will transform properly when the coordinate system is rotated.

One of the main quantities of interest are the matrix elements of a vector operator. These can measure physical properties of an atom, as well as determine decay rates. Suppose our state has definite angular momentum, but for the moment we do not assume it is an energy eigenstate. We can write the wave function as

$$\Psi(\vec{r}) = R(r)Y_{lm}(\theta, \phi) = < \vec{r}|\Psi_{lm} >$$

A typical matrix element of interest can be written

$$< \Psi'_{l'm'}|\vec{V}_i|\Psi_{lm} >$$

Selection rules are rules for that the allowed values of l', m' are, given l, m. These are most efficiently stated if instead of V_x, V_y, V_z, we use components defined as

$$V_0 = V_z, \quad V_+ = V_x + iV_y, \quad V_- = V_x - iV_y$$

Let us start by figuring out the selection rule on m'. In terms of V_0, V_+, V_-, the commutation rules are

$$[L_z, V_\pm] = \pm V_\pm, \;\; [L_z, V_0] = 0$$

Using these rules we have for example,

$$L_z V_+ |\Psi_{lm}> = ([L_z, V_+] + V_+ L_z)|\Psi_{lm}>) = (m+1)|\Psi_{lm}>,$$

so for the matrix element of V_+, we must have $m' = m+1$. Thus V_+ acts like a raising operator on L_z. Likewise V_- acts like a lowering operator on L_z, while V_0 does not change the value of L_z. To summarize, we have

$$\begin{array}{lll} m' = m+1 & for & <\Psi'_{l'm'}|V_+|\Psi_{lm}> \\ m' = m-1 & for & <\Psi'_{l'm'}|V_-|\Psi_{lm}> \\ m' = m & for & <\Psi'_{l'm'}|V_0|\Psi_{lm}> \end{array}$$

Turning to the selection rule on l', the result hinges on the *parity* of the operator $\vec{V}$. First of all let us define the parity of a state $\Psi_{lm}>$. The parity operation simply reverses $\vec{r}$, sending $\vec{r} \to -\vec{r}$. So $\mathcal{P}|\vec{r}> = |\mathcal{P}\vec{r}> = |-\vec{r}>$. Further, applying parity twice must be the same as not doing it at all, so $\mathcal{P}\mathcal{P} = \mathcal{I}$. Also we must have $\mathcal{P}^\dagger = \mathcal{P}$. To show this consider the matrix element $<\Phi|\mathcal{P}\Psi>$. We have

$$<\Phi|\mathcal{P}\Psi> = <\mathcal{P}^\dagger\Phi|\Psi> = \int d\vec{r}\Phi^*(\vec{r})\Psi(-\vec{r}) = \int d\vec{r}\Phi^*(-\vec{r})\Psi(\vec{r}) = <\mathcal{P}\Phi|\Psi>.$$

From the second and fifth equalities, we have that $\mathcal{P}^\dagger = \mathcal{P}$. Now the parity of a state $|\Psi_{lm}$ turns out to be $(-1)^l$. This is most easily shown by looking at some examples. Ignoring normalization factors and pulling a factor of r^l out of the radial wave function and writing it next to Y_{lm}, we have

Ψ_{00}	$\sim$	$f(r)$
Ψ_{11}	$\sim$	$f(r)(x+iy)$
Ψ_{10}	$\sim$	$f(r)z$
Ψ_{1-1}	$\sim$	$f(r)(x-iy)$
Ψ_{22}	$\sim$	$f(r)(x+iy)^2$
Ψ_{21}	$\sim$	$f(r)(x+iy)z$
Ψ_{20}	$\sim$	$f(r)(-2z^2+x^2+y^2)$
Ψ_{2-1}	$\sim$	$f(r)(x-iy)z$
Ψ_{2-2}	$\sim$	$f(r)(x-iy)^2$
$\vdots$	$\vdots$	$\vdots$

Note: The results in this table follow from $r^l Y_{ll} \sim (x+iy)^l$, and the use of Eq.(**??**). From the table we clearly see that reversing x, y, z leads to a factor $(-1)^l$, which shows that the parity of $\Psi_{lm}>$ is $(-1)^l$. Applying this to the matrix element

$$<\Psi'_{l'm'}|\vec{V}_i|\Psi_{lm}>,$$

we have

$$< \Psi'_{l'm'}|\vec{V}_i|\Psi_{lm} >=< \mathcal{P}\Psi'_{l'm'}|\mathcal{P}\vec{V}_i|\Psi_{lm} >= (-1)^{l'} < \Psi'_{l'm'}|\mathcal{P}\vec{V}_i\mathcal{P}|\Psi_{lm} > (-1)^l.$$

Now suppose $\vec{V}$ is an *ordinary* vector, such as $\vec{X}$ or $\vec{P}$. Then we have $\mathcal{P}\vec{V}_i\mathcal{P} = -V_i$, and the conservation of parity requires

$$(-1)^{l'}(-1)^{l+1} = 1, \quad ordinary \;\; vector$$

For an *axial* vector like $\vec{L}$, we have $\mathcal{P}\vec{V}_i\mathcal{P} = V_i$, and the conservation of parity requires

$$(-1)^{l'}(-1)^{l} = 1, \quad axial \;\; vector$$

For an ordinary vector conservation of parity alone would allow

$$l' = l \pm 1, l \pm 3, l \pm 5, \ldots,$$

and for an axial vector

$$l' = l, l \pm 2, l \pm 4, \ldots,$$

would be allowed.

The actual selection rules are more restrictive. The correct selection rules are

$$l' = l \pm 1, \quad ordinary \;\; vector$$

$$l' = l, \quad axial \;\; vector.$$

The origin of these more restrictive rules is angular momentum conservation. A vector operator carries angular momentum 1, and the application of $\vec{V}$ to a state $|\Psi_{lm} >$ can only lead to angular momenta which would come from adding angular momentum 1 to angular momentum l, namely $l+1, l, |l-1|$. This can be shown using advanced techniques in angular momentum theory, but it can also be understood with elementary methods. Suppose our vector operator is the vector $\vec{R}$, with components $R_1 = X + iY, R_0 = Z, R_{-1} = X - iY$, and we have a state $|\Psi_{lm} >$ with wave function $< \vec{r}|\Psi_{lm} >= R(r)Y_{lm}(\theta,\phi)$. Applying $\vec{R}$ to this state, we have

$$\begin{aligned} < \vec{r}|R_1|\Psi_{lm} > &= \sin(\theta)e^{i\phi}Y_{lm}(\theta,\phi)rR(r) \\ < \vec{r}|R_0|\Psi_{lm} > &= \cos(\theta)Y_{lm}(\theta,\phi)rR(r) \\ < \vec{r}|R_1|\Psi_{lm} > &= \sin(\theta)e^{-i\phi}Y_{lm}(\theta,\phi)rR(r) \end{aligned}$$

Now the trigonometric factors multiplying Y_{lm} are up to trivial factors just Y_{11}, Y_{10}, Y_{1-1}. The products $Y_{11}Y_{lm}$, etc can themselves be expanded in spherical harmonics, and the rules for combining angular momenta must be obeyed, so the resulting total angular momenta can only be $l, l{\pm}1$, but parity rules out all but $l{\pm}1$. This establishes the selection rule above for the vector operator $\vec{R}$. Similar arguements work for the momentum operator $\vec{P}$. More complicated vector operators can be constructed such as the one that occurs in the Runge-Lenz vector,

$$V_j \equiv \epsilon_{jkl}(L_k P_l - P_k L_l).$$

This operator is a rotational vector and reverses sign under parity. Since $\vec{L}$ cannot change the value of l, it is clear that this operator as well can only lead to $l' = l \pm 1$.

Finally, the only axial vector available is $\vec{L}$ itself. But acting on a state of definite l, $\vec{L}$ can only remain in the same angular momentum state, so $l' = l$ is obeyed here. In more general problems involving spin as well as several particles, more general arguments based on the general theory of the rotation group are used. However, the selection rules established here are correct for much more general cases of ordinary and axial vector operators.