12.13: Forbidden Transitions

Atomic transitions which are forbidden by the electric dipole selection rules ([e13.133]) and ([e13.134]) are unsurprisingly known as *forbidden transitions*. It is clear from the analysis in Section 1.8 that a forbidden transition is one for which the matrix element $\langle f|\epsilon\cdot\mathbf{p}|i\rangle$ is zero. However, this matrix element is only an approximation to the true matrix element for radiative transitions, which takes the form $\langle f|\epsilon\cdot\mathbf{p}\,\exp(\,{\rm i}\,\mathbf{k}\cdot\mathbf{r})|i\rangle$. Expanding $\exp(\,{\rm i}\,\mathbf{k}\cdot\mathbf{r})$, and keeping the first two terms, the matrix element for a forbidden transition becomes

$$\langle f|\epsilon\cdot\mathbf{p}\,\exp(\,{\rm i}\,\mathbf{k}\cdot\mathbf{r})|i\rangle \simeq {\rm i}\,\langle f|(\epsilon\cdot\mathbf{p})\,(\mathbf{k}\cdot\mathbf{r})|i\rangle. \tag{12.13.1}$$

Hence, if the residual matrix element on the right-hand side of the previous expression is non-zero then a “forbidden” transition can take place, albeit at a much reduced rate. In fact, in Section 1.9, we calculated that the typical rate of an electric dipole transition is

$$w_{i\rightarrow f} \sim \alpha^{\,3}\,\omega_{if}. \tag{12.13.2}$$

Because the transition rate is proportional to the square of the radiative matrix element, it is clear that the transition rate for a forbidden transition enabled by the residual matrix element ([e13.146]) is smaller than that of an electric dipole transition by a factor $(k\,r)^{\,2}$. Estimating r as the Bohr radius, and k as the wavenumber of a typical spectral line of hydrogen, it is easily demonstrated that

$$w_{i\rightarrow f} \sim \alpha^{\,5}\,\omega_{if} \tag{12.13.3}$$

for such a transition. Of course, there are some transitions (in particular, the $2S\rightarrow 1S$ transition) for which the true radiative matrix element $\langle f|\epsilon\cdot\mathbf{p}\,\exp(\,{\rm i}\,\mathbf{k}\cdot\mathbf{r})|i\rangle$ is zero. Such transitions are absolutely forbidden.

Finally, it is fairly obvious that excited states which decay via forbidden transitions have much longer life-times than those which decay via electric dipole transitions. Because the natural width of a spectral line is inversely proportional to the life-time of the associated decaying state, it follows that spectral lines associated with forbidden transitions are generally much sharper than those associated with electric dipole transitions.

Contributors and Attributions

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