## 11.6: Degenerate Perturbation Theory

Let us, rather naively, investigate the Stark effect in an excited (i.e., $n>1$) state of the hydrogen atom using standard non-degenerate perturbation theory. We can write

$$H_0\,\psi_{nlm} = E_n\,\psi_{nlm}, \tag{11.6.1}$$

because the energy eigenstates of the unperturbed Hamiltonian only depend on the quantum number $n$. Making use of the selection rules ([e12.63]) and ([e12.73]), non-degenerate perturbation theory yields the following expressions for the perturbed energy levels and eigenstates [see Equations ([e12.56]) and ([e12.57])]:

$$E'_{nl} = E_n + e_{nlnl} + \sum_{n',l'=l\pm1} \frac{|e_{n'l'nl}|^2}{E_n - E_{n'}}, \tag{11.6.2}$$

and

$$\psi'_{nlm} = \psi_{nlm} + \sum_{n',l'=l\pm1} \frac{e_{n'l'nl}}{E_n - E_{n'}}\,\psi_{n'l'm}, \tag{11.6.3}$$

where

$$e_{n'l'nl} = \langle n', l', m|H_1|n, l, m\rangle. \tag{11.6.4}$$

Unfortunately, if $n>1$ then the summations in the previous expressions are not well defined, because there exist non-zero matrix elements, $e_{nl'nl}$, that couple degenerate eigenstates: that is, there exist non-zero matrix elements that couple states with the same value of $n$, but different values of $l$. These particular matrix elements give rise to singular factors $1/(E_n - E_n)$ in the summations. This does not occur if $n=1$ because, in this case, the selection rule $l' = l\pm1$ , and the fact that $l=0$ (because $0\leq l<n$), only allow $l'$ to take the single value 1. Of course, there is no $n=1$ state with $l'=1$. Hence, there is only one coupled state corresponding to the eigenvalue $E_1$. Unfortunately, if $n>1$ then there are multiple coupled states corresponding to the eigenvalue $E_n$.

Note that our problem would disappear if the matrix elements of the perturbed Hamiltonian corresponding to the same value of $n$, but different values of $l$, were all zero: that is, if

$$\langle n, l', m|H_1|n, l, m\rangle = \lambda_{nl}\,\delta_{ll'}. \tag{11.6.5}$$

In this case, all of the singular terms in Equations ([e12.88]) and ([e12.89]) would reduce to zero. Unfortunately, the previous equation is not satisfied in general. Fortunately, we can always redefine the unperturbed eigenstates corresponding to the eigenvalue $E_n$ in such a manner that Equation ([e12.91]) is satisfied. Suppose that there are $N_n$ coupled eigenstates belonging to the eigenvalue $E_n$. Let us define $N_n$ new states which are linear combinations of our $N_n$ original degenerate eigenstates:

$$\psi^{(1)}_{nlm} = \sum_{k=1,N_n} \langle n, k, m|n, l^{(1)}, m\rangle\,\psi_{nkm}. \tag{11.6.6}$$

Note that these new states are also degenerate energy eigenstates of the unperturbed Hamiltonian, $H_0$, corresponding to the eigenvalue $E_n$. The $\psi^{(1)}_{nlm}$ are chosen in such a manner that they are also eigenstates of the perturbing Hamiltonian, $H_1$: that is, they are simultaneous eigenstates of $H_0$ and $H_1$. Thus,

$$H_1\,\psi^{(1)}_{nlm} = \lambda_{nl}\,\psi^{(1)}_{nlm}. \tag{11.6.7}$$

The $\psi^{(1)}_{nlm}$ are also chosen so as to be orthonormal: that is,

$$\langle n, l'^{(1)}, m|n, l^{(1)}, m\rangle = \delta_{ll'}. \tag{11.6.8}$$

It follows that

$$\langle n, l'^{(1)}, m|H_1|n, l^{(1)}, m\rangle = \lambda_{nl}\,\delta_{ll'}. \tag{11.6.9}$$

Thus, if we use the new eigenstates, instead of the old ones, then we can employ Equations ([e12.88]) and ([e12.89]) directly, because all of the singular terms vanish. The only remaining difficulty is to determine the new eigenstates in terms of the original

ones.

Now [see Equation ([e12.20])]

$$\sum_{l=1,N_n} |n,l,m\rangle\langle n,l,m| \equiv 1, \tag{11.6.10}$$

where 1 denotes the identity operator in the sub-space of all coupled unperturbed eigenstates corresponding to the eigenvalue $E_n$. Using this completeness relation, the eigenvalue equation ([e12.93]) can be transformed into a straightforward matrix equation:

$$\sum_{l''=1,N_n} \langle n,l',m|H_1|n,l'',m\rangle \, \langle n,l'',m|n,l^{(1)},m\rangle = \lambda_{nl} \, \langle n,l',m|n,l^{(1)},m\rangle. \tag{11.6.11}$$

This can be written more transparently as

$$\mathbf{U}\,\mathbf{x} = \lambda\,\mathbf{x}, \tag{11.6.12}$$

where the elements of the $N_n \times N_n$ Hermitian matrix $\mathbf{U}$ are

$$U_{jk} = \langle n,j,m|H_1|n,k,m\rangle. \tag{11.6.13}$$

Provided that the determinant of $\mathbf{U}$ is non-zero, Equation ([e12.100]) can always be solved to give $N_n$ eigenvalues $\lambda_{nl}$ (for $l = 1$ to $N_n$), with $N_n$ corresponding eigenvectors $\mathbf{x}_{nl}$. The normalized eigenvectors specify the weights of the new eigenstates in terms of the original eigenstates: that is,

$$(\mathbf{x}_{nl})_k = \langle n,k,m|n,l^{(1)},m\rangle, \tag{11.6.14}$$

for $k = 1$ to $N_n$. In our new scheme, Equations ([e12.88]) and ([e12.89]) yield

$$E'_{nl} = E_n + \lambda_{nl} + \sum_{n'\neq n, l'=l\pm 1} \frac{|e_{n'l'nl}|^2}{E_n - E_{n'}}, \tag{11.6.15}$$

and

$$\psi^{(1)'}_{nlm} = \psi^{(1)}_{nlm} + \sum_{n'\neq n, l'=l\pm 1} \frac{e_{n'l'nl}}{E_n - E_{n'}}\,\psi_{n'l'm}. \tag{11.6.16}$$

There are no singular terms in these expressions, because the summations are over $n' \neq n$: that is, they specifically exclude the problematic, degenerate, unperturbed energy eigenstates corresponding to the eigenvalue $E_n$. Note that the first-order energy shifts are equivalent to the eigenvalues of the matrix equation ([e12.100]).

## Contributors and Attributions


- Richard Fitzpatrick (Professor of Physics, The University of Texas at Austin)