20.3 A Primer in Perturbation Theory

The purpose of this section is to familiarize you with two basic results in perturbation theory. The first of these results was actually anticipated in our discussion of the Hellmann-Feynman lemma; the second was not. These results are derived in detail in chapter 25, where they are also extended in a number of directions. Here we just state them so they can be used to discuss the application of addition of angular momentum to the hydrogen atom.

In perturbation theory we have a Hamiltonian $\hat{H}^{(0)}$ that we assume is well understood—that is, we know its eigenstates $|k^{(0)}\rangle$ and eigenvalues $E_k^{(0)}$:

$$\hat{H}^{(0)}|k^{(0)}\rangle = E_k^{(0)}|k^{(0)}\rangle. \tag{20.3.1}$$

The "zero" superscripts indicate that these quantities are all *unperturbed*. We now consider adding a perturbation δH to the original Hamiltonian, giving us a total Hamiltonian $\hat{H}$:

$$\hat{H} = \hat{H}^{(0)} + \delta H. \tag{20.3.2}$$

The perturbation δH is a Hermitian operator. It usually makes the total Hamiltonian very complicated to analyze exactly. In perturbation theory the idea is to find approximate energies and approximate eigenstates of $\hat{H}$ when the perturbation δH is small. It turns out that one must distinguish two cases: it makes a difference if we are looking at a nondegenerate state or at a set of degenerate states. While the treatment of nondegenerate states is easier, for the hydrogen atom the unperturbed energy levels are highly degenerate, so we face a more intricate situation.

Case 1: Nondegenerate energy level Assume the state $|k^{(0)}\rangle$ with energy $E_k^{(0)}$ is not degenerate. In this case the perturbation changes the state and the energy. Calling the energy of the perturbed state E_k, we write

$$E_k = E_k^{(0)} + \delta E_k + \mathcal{O}(\delta H^2). \tag{20.3.3}$$

Here, $E_k^{(0)}$ is the energy of the state absent the perturbation, and δE_k is the correction to the energy to first order in δH. The $\square(\delta H^2)$ term indicates that there are higher-order corrections. It is a very nice fact that finding the energy correction does not require finding how the state changes! Indeed, we find that

$$\delta E_k = \langle k^{(0)} | \delta H | k^{(0)} \rangle. \tag{20.3.4}$$

The correction to the energy is just the expectation value of the perturbation δH on the *unperturbed* state $|k^{(0)}\rangle$. Since the state is assumed known, this is a very simple result. It is sometimes said that this is the most important result in perturbation theory! We actually derived this result in example 7.3, as an application of the Hellman-Feynman lemma.

Case 2: A degenerate energy level Suppose we have a degenerate energy level of energy $E_n^{(0)}$ with N degenerate eigenstates $|n^{(0)}; l\rangle$ with $l = 1, \ldots, N$, chosen to be orthonormal:

$$\text{Energy } E_n^{(0)} \text{ states: } |n^{(0)}; 1\rangle, \ldots, |n^{(0)}; N\rangle. \tag{20.3.5}$$

To proceed, one calculates the $N \times N$ matrix $[\delta H]$ representing the operator δH in the degenerate subspace. The matrix elements are

$$\delta H_{ij} \equiv \langle n^{(0)}; i|\delta H|n^{(0)}; j\rangle \tag{20.3.6}$$

and can be calculated explicitly. The $N \times N$ matrix $[\delta H]$ must now be diagonalized to find the N eigenvectors $|\psi_I^{(0)}\rangle$, labeled by I, with their associated eigenvalues δE_{nI}:

$$[\delta H]\,|\psi_I^{(0)}\rangle = \delta E_{nI}\,|\psi_I^{(0)}\rangle, \quad I = 1, \ldots, N. \tag{20.3.7}$$

If you find an eigenvector in component form, the associated state is immediately constructed:

$$\text{eigenvector: } \begin{pmatrix} a_{I1}^{(0)} \\ \vdots \\ a_{IN}^{(0)} \end{pmatrix} \quad \Rightarrow \quad |\psi_I^{(0)}\rangle = \sum_k |n^{(0)}; k\rangle a_{Ik}^{(0)}. \tag{20.3.8}$$

Before the perturbation is included, the N degenerate states are on the same footing. After the perturbation is included, the zeroth-order approximation to the new energy eigenstates are the $|\psi_I^{(0)}\rangle$. They are zeroth order because, while selected by the perturbation, the coefficients a_I are not proportional to δH. The energy correction for $|\psi_I^{(0)}\rangle$ is in fact the eigenvalue δE_{nI}, and therefore the total energy E_{nI} of the state $|\psi_I^{(0)}\rangle$ is

$$E_{nI} = E_n^{(0)} + \delta E_{nI} + \mathcal{O}(\delta H^2). \tag{20.3.9}$$

In specific situations, it is sometimes possible to choose a basis in the degenerate subspace for which $[\delta H]$ is diagonal. Such a basis is called a *good basis*. The basis vectors are then the zeroth-order energy eigenstates, and the energy corrections are precisely the elements in the diagonal of $[\delta H]$. In the problems we will consider, with two angular momenta, the eigenstates of the *total* angular momenta will provide a good basis.