3 Dealing with Degeneracy

3.1 Time-Independent Degenerate Perturbation Theory

We have seen how we can find approximate solutions for a system whose Hamiltonian is of the form

$$\hat{H} = \hat{H}_0 + \hat{V}$$

When we assumed that $\hat{H}$ and $\hat{H}_0$ possess discrete, non-degenerate eigenvalues only. This led to a mixing of states where

$$|\phi_0\rangle = |n_0\rangle + \sum_{k \neq 0} \frac{V_{k0}}{(E_0 - E_k)} |n_k\rangle$$

Clearly, if $E_0 = E_k$ this diverges. As do the higher order energy shifts (see 2.4). Thus for the degenerate case we cannot associate a particular perturbed state $|\phi_0\rangle$ with a particular unperturbed state $|n_0\rangle$: we need to take a different approach. In fact, the approximation we make is completely different: we assume that the small perturbation *only mixes those states which are degenerate.* We then solve the problem exactly for that subset of states.

Assume that $\hat{H}_0$ possesses N degenerate eigenstates $|m\rangle$ with eigenvalue E_{deg}. It may also possesses non-degenerate eigenstates, which can be treated separately by non-degenerate perturbation theory. We write a perturbed eigenstate $|\phi_j\rangle$ as an linear expansion in the unperturbed degenerate eigenstates only:

$$|\phi_j\rangle = \sum_i |m_i\rangle\langle m_i|\phi_j\rangle = \sum_i c_{ji}\, |m_i\rangle$$

Where i here runs over degenerate states only. The TISE now becomes:

$$[\hat{H}_0 + \hat{V}]\, |\phi_j\rangle = [\hat{H}_0 + \hat{V}] \sum_i c_{ji}\, |m_i\rangle = E_j \sum_i c_{ji}\, |m_i\rangle$$

but we know that for all degenerate eigenstates $\hat{H}_0 |m_i\rangle = E_{deg}\, |m_i\rangle$. So we obtain:

$$\sum_i c_{ji}\, \hat{V} |m_i\rangle = (E_j - E_{deg}) \sum_i c_{ji}\, |m_i\rangle$$

premultiplying by some unperturbed state $\langle m_k|$ gives

$$\sum_i c_{ji} \left[\langle m_k|\hat{V}|m_i\rangle - \delta_{ik}(E_j - E_{deg}) \right] = 0$$

We can get a similar equation from each unperturbed state $|m_k\rangle$. We thus have an eigenvalue problem: the eigenvector has elements c_{ji} and the eigenvalues are $\Delta E_j = E_j - E_{deg}$. Writing the matrix elements between the i^{th} and k^{th} unperturbed degenerate states as $V_{ik} \equiv \langle m_i|\hat{V}|m_k\rangle$ we recover the determinantal equation:

$$\begin{vmatrix} V_{11} - \Delta E_j & V_{12} & \ldots & V_{1N} \\ V_{21} & V_{22} - \Delta E_j & \ldots & V_{2N} \\ \ldots & \ldots & \ldots & \ldots \\ V_{N1} & V_{N2} & \ldots & V_{NN} - \Delta E_j \end{vmatrix} = 0$$

The N eigenvalues obtained by solving this equation give the shifts in energy due to the perturbation, and the eigenvectors give the perturbed states $|\phi\rangle$ in the unperturbed, degenerate basis set $|m\rangle$.

3.2 Notes

- The perturbed eigenstates of $\hat{H}$ are linear combinations of degenerate eigenstates of $\hat{H}_0$. This means that they too are eigenstates of $\hat{H}_0$ from a different eigenbasis.

- If $\hat{H}_0$ is compatible with $\hat{V}$, i.e. $[\hat{H}_0, \hat{V}] = 0$, then there is no mixing with non-degenerate states and the analysis above is exact.

- Notice how the mathematics mimics the quantum mechanics. Without the perturbation the eigenbasis of $\hat{H}_0$ is not unique. When we try to determine its energy shift we find a matrix equation which can *only* be solved for *specific* values of ΔE_j. These ΔE_j in turn correspond to specific choices for the coefficients c_{ji}, i.e. particular linear combinations of the unperturbed states. Thus to solve the equations we are forced to collapse the wavefunction onto an eigenstate of $\hat{V}$. V_{ki} is a Hermitian matrix, and consequently has real eigenvalues.

3.3 Example of degenerate perturbation theory: Stark Effect in Hydrogen

The change in energy levels in an atom due to an external electric field is known as the Stark effect. The perturbing potential is thus $\hat{V} = eEz = eEr\cos\theta$. Ignoring spin, we examine this effect on the fourfold degenerate n=2 levels. We will label these by their appropriate quantum number: $|l, m\rangle$.

$$u_{00} = (8\pi a_0^3)^{-1/2}(1 - r/2a_0)e^{-r/2a_0}; \qquad u_{10} = (8\pi a_0^3)^{-1/2}(r/2a_0)\cos\theta e^{-r/2a_0}$$

$$u_{11} = (\pi a_0^3)^{-1/2}(r/8a_0)\sin\theta e^{i\phi}e^{-r/2a_0} \qquad u_{1-1} = (\pi a_0^3)^{-1/2}(r/8a_0)\sin\theta e^{-i\phi}e^{-r/2a_0}$$

From the analysis above, we need to calculate the matrix elements.

$$V_{lm,l'm'} = \langle l, m|eEz|l', m'\rangle = eE\int\int\int u_{lm}^*(r\cos\theta)u_{l'm'}r^2\sin\theta d\theta d\phi dr$$

It turns out that many of these are zero, since if any of the integrals are zero their product will be. Looking first at parity, it is clear that eEz has odd parity $(eE(r)\cos(\pi - \theta) = -eEr\cos\theta)$, u_{00} has even parity and u_{1m} have odd parity. Since the integral over all space of any odd function is zero, $V_{00,00} = V_{1m,1m'} = 0$. Secondly, $\int_0^{2\pi} e^{\pm i\phi}d\phi = 0$, so $V_{00,11} = V_{00,1-1} = V_{11,00} = V_{1-1,00} = 0$.

Since the perturbation is real, $V_{00,10} = V_{10,00}$ and the only remaining non-zero matrix element is:

$$\langle 00|eEr\cos\theta|10\rangle = (8\pi a_0^3)^{-1}\int_0^{2\pi} d\phi\int_0^{\pi}\cos^2\theta\sin\theta d\theta\int_0^{\infty}(1 - r/2a_0)e^{-r/a_0}r^4/2a_0 dr = -3eEa_0$$

This is best solved as a matrix problem, the determinantal equation is then:

$$\begin{vmatrix} -\Delta E & -3eEa_0 & 0 & 0 \\ -3eEa_0 & -\Delta E & 0 & 0 \\ 0 & 0 & -\Delta E & 0 \\ 0 & 0 & 0 & -\Delta E \end{vmatrix} = (\Delta E)^4 - (\Delta E)^2(3eEa_0)^2 = 0$$

The solutions to this are $\Delta E = \pm 3eEa_0, 0, 0$. The degeneracy of the states u_{11} and u_{1-1} is not lifted, but the new non-degenerate eigenstates corresponding to $\Delta E_n = \pm 3eEa_0$ are mixtures, $(u_{00} \mp u_{10})/\sqrt{2}$. Consequently, the spectral line corresponding to the $n = 2 \rightarrow n = 1$ Lyman-α transition is split into three if the hydrogen atom is in an electric field.

A curious aspect of these eigenstates is that they are not eigenstates of $\mathbf{L^2}$, although they are eigenstates of L_z. Nor do they have definite parity. In an electric field, therefore, the total angular momentum is not a good quantum number. Note that this effect is specific to hydrogen, since in other elements the s and p levels are not degenerate.

Experimental results confirm this theory beautifully - the splitting of levels in hydrogen varies linearly with the applied field strength, while in all other atoms it varies quadratically: the first order perturbation is zero.

Looking at the electrostatics: the energy of a spherically symmetric charge density in a uniform field is clearly independent of orientation. To have any orientation dependence the object must have a dipole moment. The combination of 2s and 2p wavefunctions achieves this.

3.4 Symmetry and Degeneracy

In real systems degeneracy almost always related to symmetry. In general if the probability density has lower symmetry than the Hamiltonian, the wavefunction will be degenerate.

There is a clear physical reason behind this. Consider the $2p_x$ orbital in hydrogen: it has a lobe along the x-axis. However, there is no measurable quantity which defines an x-axis - the coordinate system is just introduced by physicists to help solve the equations. The lobe could just as well point in the y or z or $(27, 43.2, -12)$ direction. Thus the p_x orbital has lower symmetry than the Hamiltonian (spherically symmetric potential), and is degenerate with p_y and p_z. Likewise the spin: we talk about 'spin up', but there is no way to define 'up' from the Hamiltonian. Thus there is degeneracy between spin states 'up' and 'down'.

If we reduce the symmetry of the Hamiltonian, we now 'lift' the degeneracy. (i.e. the levels no longer have the same energy). For example, an applied magnetic field defines an axis and lowers the symmetry of the Hamiltonian. If the field is weak, we can use perturbation theory and assume we still have p orbitals (Zeeman effect). Now, the orbitals must be eigenstates not only of $\hat{H}_0$, but also of $\mu.\mathbf{B}$ where μ is the magnetic dipole moment. The degenerate energy level splits into several different energy levels, depending on the relative orientation of the moment and the field: The degeneracy is lifted by the reduction in symmetry.

3.5 Time-variation of expectation values: Degeneracy and constants of motion

The time variation of the expectation value of an operator $\hat{A}$ which commutes with the Hamiltonian is:

$$\frac{d}{dt}\langle\Phi|\hat{A}|\Phi\rangle = \int d^3r \frac{d\Phi^*}{dt}\hat{A}\Phi + \Phi^*\hat{A}\frac{d\Phi}{dt}$$

but since $\quad i\hbar\frac{d\Phi}{dt} = \hat{H}\Phi$ and $-i\hbar\frac{d\Phi^*}{dt} = \hat{H}^*\Phi^*$

$$-i\hbar\frac{d}{dt}\langle\Phi|\hat{A}|\Phi\rangle = \int(\hat{H}^*\Phi^*\hat{A}\Phi - \Phi^*\hat{A}\hat{H}\Phi)d^3r = \langle\Phi|[\hat{H},\hat{A}]|\Phi\rangle$$

Where we also use the fact that $\hat{H}$ is Hermitian. Thus if $\hat{H}$ commutes with $\hat{A}$ ($[\hat{H},\hat{A}] = 0$), the expectation value of A is independent of time. It is a conserved quantity.

As we have seen above, if we have degenerate eigenstates of the Hamiltonian, $\hat{H}$, then there must be some other operator $\hat{A}$ which commutes with the Hamiltonian for which there are energy-degenerate eigenstates with different eigenvalues A. These eigenvalues, A, are then constants of the motion. Moreover, if Φ is an eigenfunction of $\hat{H}$, then $\hat{A}\Phi$ is also an eigenfunction of $\hat{H}$.

$$\hat{H}(\hat{A}\Phi) = \hat{A}\hat{H}\Phi = \hat{A}(E\Phi) = E(\hat{A}\Phi)$$

There is a three way link between symmetry, degeneracy and conserved quantities.

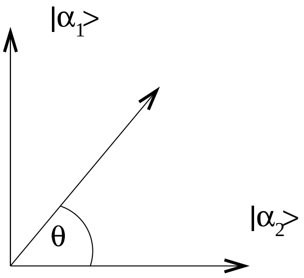

Figure 1: Any linear combination of two degenerate eigenstates produces another eigenstate.

3.6 Wavefunction Collapse onto degenerate levels

Refer back to the postulates of quantum mechanics: We know that acting with an operator $\hat{A}$ on an eigenstate $|\alpha_n\rangle$ of that operator gives us an eigenvalue A_n, which corresponds to a measurable quantity.

There is no guarantee that $|\alpha_n\rangle$ is the only eigenstate of $\hat{A}$ which has this eigenvalue (e.g. energy levels in hydrogen). Different states with the same eigenvalue are referred to as degenerate.

Assume we find two orthogonal, degenerate eigenstates of $\hat{A}$: $|\alpha_1\rangle$ and $|\alpha_2\rangle$. i.e. $\hat{A}|\alpha_1\rangle = A_1|\alpha_1\rangle$ and $\hat{A}|\alpha_2\rangle = A_1|\alpha_2\rangle$. We also see that

$$\hat{A}\left(\cos\theta|\alpha_1\rangle + \sin\theta|\alpha_2\rangle\right) = A_1\left(\cos\theta|\alpha_1\rangle + \sin\theta|\alpha_2\rangle\right)$$

for any θ. We use $\cos\theta$ for the expansion instead of the normal c_i to emphasise the similarity between eigenstates and vectors. It also allows for easy normalisation since $\cos^2\theta + \sin^2\theta = 1$.

Thus any linear combination of degenerate eigenstates produces another eigenstate. There is still only twofold degeneracy, because there are only two orthogonal states, $(\sin\theta|\alpha_1\rangle - \cos\theta|\alpha_2\rangle)$ being the other one. The complete set of orthonormal eigenstates for $\hat{A}$ is thus not a unique quantity, since we can choose any θ to generate a pair of degenerate eigenstates.

A consequence of this is that when a measurement is made of $\hat{A}$ which finds A_1, there is not a complete collapse of the wavefunction.

Consider measuring observable A in a system in a general state $|\Phi\rangle$. By expanding $|\Phi\rangle$ in the eigenstates of $\hat{A}$: $|\Phi\rangle = \sum_i c_i|\alpha_i\rangle$ we find the probability that the measurement will yield result A_1 is

$$|\langle\alpha_1|\Phi\rangle|^2 + |\langle\alpha_2|\Phi\rangle|^2 \equiv |c_1|^2 + |c_2|^2$$

The measurement has determined that we are either in state α_1 or α_2, but not which. Thus there is a partial collapse of the wavefunction onto a linear combination of them:

$$(\cos\theta|\alpha_1\rangle + \sin\theta|\alpha_2\rangle); \qquad \cos\theta = \frac{c_1}{\sqrt{|c_1|^2 + |c_2|^2}}$$

which is itself an eigenvector of $\hat{A}$.

Thus, in the case of degenerate final states, the final wavefunction after the measurement *does* depend on the initial wavefunction. The generalisation of this to the case of many degenerate states is straightforward.