Angular Momentum

$[L_x, L_y] = i\hbar L_z$, $[L_y, L_z] = i\hbar L_x$, $[L_z, L_x] = i\hbar L_y$

$L^2 = L_x^2 + L_y^2 + L_z^2$, $L_\pm = L_x \pm i L_y$

$L^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$

$L_z Y_{lm} = m\hbar Y_{lm}$

$Y_{lm} = |l, m\rangle$

$\iint Y^*_{l'm'}(\theta,\phi) Y_{lm}(\theta,\phi) \sin\theta \, d\theta \, d\phi = \delta_{ll'}\delta_{mm'}$

$\downarrow$

$\langle l', m' | l, m\rangle = \delta_{ll'}\delta_{mm'}$

$L_\pm = L_x \pm i L_y$

Note it is not Hermitian

$(L_\pm)^\dagger = (L_x \pm i L_y)^\dagger$

$= L_x \mp i L_y = L_\mp$

It can be shown that

$[L^2, L_\pm] = 0$, $[L_+, L_-] = 2\hbar L_z$

$[L_z, L_\pm] = \pm\hbar L_\pm$

$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$

$L_+ L_- = (L_x + i L_y)(L_x - i L_y)$

$= L_x^2 + L_y^2 + \underbrace{i L_y L_x - i L_x L_y}_{-i[L_x, L_y] \,=\, i\hbar L_z}$

$= L_x^2 + L_y^2 + \hbar L_z$

$= L^2 - L_z^2 + \hbar L_z$

$L_- L_+ = L^2 - L_z^2 - \hbar L_z$

$$L_z(L_+ Y_{\ell m}) = (L_+ L_z + \hbar L_+) Y_{\ell m}$$

$$= L_+ m\hbar Y_{\ell m} + \hbar L_+ Y_{\ell m}$$

$$= (m\hbar + \hbar) L_+ Y_{\ell m} = (m+1)\hbar (L_+ Y_{\ell m})$$

$\therefore$ $L_+ Y_{\ell m}$ is an eigenfunction of L_z with eigenvalue $(m+1)\hbar$

$$L^2(L_+ Y_{\ell m}) = L_+ L^2 Y_{\ell m} = L_+ (\ell(\ell+1)\hbar) Y_{\ell m}$$

$$= \ell(\ell+1)\hbar^2 (L_+ Y_{\ell m}$$

$\therefore$ $L_+ Y_{\ell m}$ is an eigenfunction of L^2 with eigenvalue $\ell(\ell+1)\hbar^2$

$$\Rightarrow \quad L_+ Y_{\ell m} \quad C_{\ell m} Y_{\ell, m+1}$$

$$\iint (L_+ Y_{\ell m})^* (L_+ Y_{\ell m}) \sin\theta \, d\theta \, d\phi$$

$$= |C_{\ell m}|^2 \iint Y^*_{\ell, m+1} Y_{\ell, m+1} \sin\theta \, d\theta \, d\phi$$

$$LHS = \iint Y^*_{\ell m} L_- L_+ Y_{\ell m} \sin\theta \, d\theta \, d\phi$$

$$= \iint Y^*_{\ell m} (L^2 - L_z^2 - \hbar L_z) Y_{\ell m} \sin\theta \, d\theta \, d\phi$$

$$(\ell(\ell+1)\hbar^2 - m^2\hbar^2 - \hbar m\hbar) Y_{\ell m} \sin\theta \, d\theta \, d\phi$$

$$C_{\ell m} = \hbar \sqrt{\ell(\ell+1) - m(m+1)}$$

$$\Rightarrow \quad L Y_{\ell m} = \hbar \sqrt{\ell(\ell+1) - m(m+1)} \; Y_{\ell, m+1}$$

$$L_- Y_{\ell m} = \hbar \sqrt{\ell(\ell+1) - m(m-1)} \; Y_{\ell, m-1}$$

Spin

$$[S_i, S_j] = i\epsilon_{ijk} S_k$$

$$S^2 \left| \tfrac{1}{2}, \pm\tfrac{1}{2} \right\rangle = \underset{\downarrow}{s}(\underset{\downarrow}{s}+1)\hbar^2 \left| \tfrac{1}{2}, \pm\tfrac{1}{2} \right\rangle$$

$$\tfrac{1}{2}$$

$$S_z \left| \tfrac{1}{2}, \pm\tfrac{1}{2} \right\rangle = \pm\tfrac{1}{2}\hbar \left| \tfrac{1}{2}, \pm\tfrac{1}{2} \right\rangle$$

$$\psi_{n\ell m_\ell m_s} = \psi_{n\ell m_\ell} |s, m_s\rangle$$

THE ADDITION OF ANGULAR MOMENTA

THE ADDITION OF TWO SPINS

Suppose we have two electrons, whose spins are described by the operators $\mathbf{S}_1$ and $\mathbf{S}_2$. Each of these sets of operators satisfies the standard angular momentum commutation relations

$$[S_{1x}, S_{1y}] = i\hbar S_{1z}$$

and so on,

$$[S_{2x}, S_{2y}] = i\hbar S_{2z} \tag{15-1}$$

and so on, but the two sets of operators commute with each other, since the degrees of freedom associated with different particles are independent, that is,

$$[\mathbf{S}_1, \mathbf{S}_2] = 0 \tag{15-2}$$

Let us now define the total spin $\mathbf{S}$ by

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 \tag{15-3}$$

The commutation relations obeyed by the components of $\mathbf{S}$ are

$$\begin{aligned} [S_x, S_y] &= [S_{1x} + S_{2x}, S_{1y} + S_{2y}] \\ &= [S_{1x}, S_{1y}] + [S_{2x}, S_{2y}] \\ &= i\hbar(S_{1z} + S_{2z}) = i\hbar S_z \end{aligned} \tag{15-4}$$

and so on. We are therefore justified in calling **S** the total *spin*. We may now determine the eigenvalues and eigenfunctions of $\mathbf{S}^2$ and S_z.

The two-spin system actually has four states. If we denote the spinor of the first electron by $\chi_{\pm}^{(1)}$, so that

$$\begin{aligned} \mathbf{S}_1^2 \chi_{\pm}^{(1)} &= \tfrac{1}{2}(\tfrac{1}{2}+1)\,\hbar^2 \chi_{\pm}^{(1)} \\ S_{1z}\chi_{\pm}^{(1)} &= \pm\tfrac{1}{2}\hbar\chi_{\pm}^{(1)} \end{aligned} \tag{15-5}$$

and similarly for the spinor $\chi_{\pm}^{(2)}$ of the second electron, then the four states are

$$\chi_{+}^{(1)}\chi_{+}^{(2)},\ \chi_{+}^{(1)}\chi_{-}^{(2)},\ \chi_{-}^{(1)}\chi_{+}^{(2)},\ \chi_{-}^{(1)}\chi_{-}^{(2)} \tag{15-6}$$

The eigenvalues of S_z for the four states are

$$\begin{aligned} S_z\chi_{\pm}^{(1)}\chi_{\pm}^{(2)} &= (S_{1z}+S_{2z})\chi_{\pm}^{(1)}\chi_{\pm}^{(2)} \\ &= (S_{1z}\chi_{\pm}^{(1)})\,\chi_{\pm}^{(2)} + \chi_{\pm}^{(1)}(S_{2z}\chi_{\pm}^{(2)}) \end{aligned}$$

that is,

$$\begin{aligned} S_z\chi_{+}^{(1)}\chi_{+}^{(2)} &= \hbar\chi_{+}^{(1)}\chi_{+}^{(2)} \\ S_z\chi_{+}^{(1)}\chi_{-}^{(2)} &= S_z\chi_{-}^{(1)}\chi_{+}^{(2)} = 0 \\ S_z\chi_{-}^{(1)}\chi_{-}^{(2)} &= -\hbar\chi_{-}^{(1)}\chi_{-}^{(2)} \end{aligned} \tag{15-7}$$

There are two states with m-value 0. One might expect that one linear combination of them will form an $S = 1$ state, to form a triplet with the $m = 1$ and $m = -1$ states, and the orthogonal combination will form a singlet $S = 0$ state. To check this expectation, let us construct the lowering operator

$$S_- = S_{1-} + S_{2-} \tag{15-8}$$

and apply this to the $m = 1$ state. This should give us the $m = 0$ state that belongs to the $S = 1$ triplet, aside from a coefficient in front. Indeed, using the fact that

$$S_-^{(i)}\chi_{+}^{(i)} = \hbar\chi_{-}^{(i)} \tag{15-9}$$

which can be established by noting that

$$\tfrac{1}{2}\hbar\left[\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} - i\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\right]\begin{pmatrix}1\\ 0\end{pmatrix} = \hbar\begin{pmatrix}0\\ 1\end{pmatrix} \tag{15-10}$$

we get

$$\begin{aligned} S_-\chi_{+}^{(1)}\chi_{+}^{(2)} &= (S_{1-}\chi_{+}^{(1)})\,\chi_{+}^{(2)} + \chi_{+}^{(1)}S_{2-}\chi_{+}^{(2)} \\ &= \hbar\chi_{-}^{(1)}\chi_{+}^{(2)} + \hbar\chi_{+}^{(1)}\chi_{-}^{(2)} \\ &= \sqrt{2}\hbar\,\frac{\chi_{+}^{(1)}\chi_{-}^{(2)} + \chi_{-}^{(1)}\chi_{+}^{(2)}}{\sqrt{2}} \end{aligned} \tag{15-11}$$

The linear combination has been normalized, and the compensating factor in front, $\sqrt{2}\hbar$, agrees with what one would expect from (11-36) and (11-48) with $l = m = 1$. If we now apply S_- to this linear combination, and note that

$$S_-^{(i)}\chi_-^{(i)} = 0 \tag{15-12}$$

we get

$$\begin{aligned} S_- \frac{\chi_+^{(1)}\chi_-^{(2)} + \chi_-^{(1)}\chi_+^{(2)}}{\sqrt{2}} &= \frac{\hbar}{\sqrt{2}}(\chi_-^{(1)}\chi_-^{(2)} + \chi_-^{(1)}\chi_-^{(2)}) \\ &= \sqrt{2}\hbar\chi_-^{(1)}\chi_-^{(2)} \end{aligned} \tag{15-13}$$

as we should, for an angular momentum state $S = 1$. The remaining state, constructed to be orthogonal to (15-11) and properly normalized, is

$$\frac{1}{\sqrt{2}}(\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}) \tag{15-14}$$

and because it has no partners, we conjecture that it is an $S = 0$ state. In order to check this, we compute $\mathbf{S}^2$ for the two states

$$X_\pm = \frac{1}{\sqrt{2}}(\chi_+^{(1)}\chi_-^{(2)} \pm \chi_-^{(1)}\chi_+^{(2)}) \tag{15-15}$$

We have

$$\begin{aligned} \mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 &= \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2 \\ &= \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2S_{1z}S_{2z} + S_{1+}S_{2-} + S_{1-}S_{2+} \end{aligned} \tag{15-16}$$

First of all,

$$\begin{aligned} \mathbf{S}_1^2 X_\pm &= \frac{1}{\sqrt{2}}(\chi_-^{(2)}\mathbf{S}_1^2\chi_+^{(1)} \pm \chi_+^{(2)}\mathbf{S}_1^2\chi_-^{(1)}) \\ &= \tfrac{3}{4}\hbar^2 X_\pm \end{aligned} \tag{15-17}$$

and similarly

$$\mathbf{S}_2^2 X_\pm = \tfrac{3}{4}\hbar^2 X_\pm \tag{15-18}$$

Next, we calculate

$$2S_{1z}S_{2z}X_\pm = 2(\tfrac{1}{2}\hbar)(-\tfrac{1}{2}\hbar)\, X_\pm = -\tfrac{1}{2}\hbar^2 X_\pm \tag{15-19}$$

Finally

$$\begin{aligned} (S_{1+}S_{2-} + S_{1-}S_{2+})\, X_\pm = \frac{1}{\sqrt{2}}(&S_{1+}\chi_+^{(1)}S_{2-}\chi_-^{(2)} + S_{1-}\chi_+^{(1)}S_{2+}\chi_-^{(2)} \\ &\pm S_{1+}\chi_-^{(1)}S_{2-}\chi_+^{(2)} \pm S_{1-}\chi_-^{(1)}S_{2+}\chi_+^{(2)}) \end{aligned}$$

which, with the help of (15-9) and (15-12) yields

$$(S_{1+}S_{2-} + S_{1-}S_{2+})\, X_{\pm} = \pm\hbar^2 X_{\pm} \tag{15-20}$$

Thus

$$\begin{aligned} \mathbf{S}^2 X_{\pm} &= \hbar^2(\tfrac{3}{4} + \tfrac{3}{4} - \tfrac{1}{2} \pm 1)\, X_{\pm} = \begin{pmatrix} 2 \\ 0 \end{pmatrix} \hbar^2 X_{\pm} \\ &= \hbar^2 S(S+1)\, X_{\pm} \end{aligned} \tag{15-21}$$

with $S = 1$ and 0 corresponding to the $\pm$ states.

What we have shown is that the totality of the four states of two spin 1/2 particles may be recombined into a triplet and into a singlet total spin state. It is important to note that the two descriptions are entirely equivalent. In one case we have as our complete set of commuting observables $\mathbf{S}_1^2$, $\mathbf{S}_2^2$, S_{1z}, and S_{2z}. In the other case we have as our complete set of commuting observables $\mathbf{S}^2$, S_z, $\mathbf{S}_1^2$, $\mathbf{S}_2^2$. By the expansion theorem, any function can be expanded in terms of a complete set of eigenstates. *What we have demonstrated here is the expansion of the eigenstates of the second set of observables in terms of the complete set of states of the first set of observables.* This is quite analogous to the expression of the eigenstates of the hydrogen atom in terms of the eigenstates of the momentum operator, in which the coefficients (the analogs of the $1/\sqrt{2}$'s here) are the momentum-space wave functions. It is a simple exercise to invert the process and to find the products of the $\chi^{(1)}\chi^{(2)}$ in terms of triplet and singlet combinations.

In physical problems it frequently happens that to first approximation two sets of completely commuting observables are equally useful in the construction of eigenstates. In next approximation, when additional terms in the Hamiltonian are taken into account, only one of these sets remains useful. A simple example occurs in low energy nuclear physics.

Angular momentum

The eigenequation associated with angular momentum reads

$$\hat{\mathbf{L}}^2 Y(\theta,\phi) = 2mr^2 E_L(r) Y(\theta,\phi) = \text{const} \cdot Y(\theta,\phi) \tag{20-1}$$

where $2mr^2E_L$ is the eigenvalue, and

$$\hat{\mathbf{L}}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\theta^2}\right) \tag{20-2}$$

Similar to the HO problem, we can proceed in two ways. We can either:

1. solve the differential equation using some Taylor expansion.
2. we can take a more abstract operator approach.

Here we will do the latter. (For the direct approach see *Gasiorowicz*, supplement *7-B*, or *F&T*.) We analyze the commutation relations for the angular momentum operator

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} \tag{20-3}$$

Note. that since waves in orthogonal directions are independent, we have no Heisenberg uncertainty restriction on, say x and p_y, and consequently the commutator is zero, $[x, p_y] = 0$.

Let us calculate the commutator between different components of $\mathbf{L}$: omit operator symbol

$$\begin{aligned}
[L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] && (20\text{-}4)\\
&= y[p_z, z]p_x + x[z, p_y]p_y && (20\text{-}5)\\
&= \frac{\hbar}{i} yp_x + i\hbar x p_y && (20\text{-}6)\\
&= i\hbar(xp_y - yp_x) && (20\text{-}7)\\
&= i\hbar L_z && (20\text{-}8)
\end{aligned}$$

$$\begin{aligned}
[L_x, L_y] &= i\hbar L_z && (20\text{-}9)\\
[L_y, L_z] &= i\hbar L_x && (20\text{-}10)\\
[L_z, L_x] &= i\hbar L_y && (20\text{-}11)
\end{aligned}$$

The fact that the different components of angular momentum do not commute means that it is not possible to find simultaneous eigenstates of, say, L_x and L_z, unless $L_z = 0$ for that state (see previous lecture).

What about $\mathbf{L}^2$?

$$[L_z, \mathbf{L}^2] = [L_z, L_x^2] + [L_z, L_y^2] \tag{20-12}$$
$$= L_x[L_z, L_x] + [L_z, L_x]L_x + L_y[L_z, L_y] + [L_z, L_y]L_y \tag{20-13}$$
$$= i\hbar L_x L_y + i\hbar L_y L_x - i\hbar L_y L_x - i\hbar L_x L_y \tag{20-14}$$
$$= 0 \tag{20-15}$$

This implies that one can find simultaneous eigenstates of $\mathbf{L}^2$ and one component of $\mathbf{L}^2$ and one component of $\mathbf{L}$, e.g., L_z, but not of all components:

Proof. (Direct proof by contradiction) For a simultaneous eigenstate $|n\rangle$ of L_x and L_y with

$$L_x|n\rangle = l_1|n\rangle, \tag{20-16}$$
$$L_y|n\rangle = l_2|n\rangle. \tag{20-17}$$

we have

$$[L_x, L_y]|n\rangle = 0 = L_z|n\rangle \tag{20-18}$$

and

$$l_2|n\rangle = L_y|n\rangle = \frac{1}{i\hbar}[L_z, L_x]|n\rangle = 0 \quad \rightarrow \quad l_2 = 0 \tag{20-19}$$

and similarly $l_1 = 0$. Only for $\mathbf{L} = 0$ can we have simultaneous eigenstates of L_x, L_y, L_z. □

In general, we can only have simultaneous eigenstates of $\mathbf{L}^2$ and L_z (or L_x or L_y, L_z by convention). Let us denote such an eigenstate by $|l, m\rangle$ with

$$L_z|l, m\rangle = m\hbar|l, m\rangle \tag{20-20}$$
$$\mathbf{L}^2|l, m\rangle = \hbar^2 l(l+1)|l, m\rangle \tag{20-21}$$

The reason for the strange definition of the quantum number l (or $\mathbf{L}^2$ eigenvalue $\hbar^2 l(l+1)$) will become apparent later. m, l are dimensionless numbers, since $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ has units of $\hbar$. We assume that the simultaneous eigenstates of $\mathbf{L}^2$ and L_z are normalized,

$$\boxed{\langle l', m'|l, m\rangle = \delta_{ll'}\delta_{mm'}} \quad \rightarrow \quad \begin{array}{c}\text{orthonormality for} \\ \text{angular momentum} \\ \text{eigenstates}\end{array} \tag{20-22}$$

Raising and lowering operators for angular momentum

It is useful to define the following non-Hermitian operators

$$\boxed{L_\pm = L_x \pm iL_y} \tag{20-23}$$

$$\boxed{L_+^\dagger = L_-} \tag{20-24}$$

$$\boxed{L_-^\dagger = L_+} \tag{20-25}$$

L_+ and L_- are Hermitian conjugate of each other (reminiscent of $\hat{a} = \frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0}$, $\hat{a}^\dagger = \frac{\hat{x}}{x_0} - i\frac{\hat{p}}{p_0}$). To understand similar significance of these operators, let us analyze their commutation relations:

$$\boxed{[\mathbf{L}^2, L_\pm] = 0} \tag{20-26}$$

since $[\mathbf{L}^2, L_x] = 0$, $[\mathbf{L}^2, L_y] = 0$.

$$\begin{aligned}
[L_+, L_-] &= [L_x + iL_y, L_x - iL_y] && (20\text{-}27)\\
&= -i[L_x, L_y] + i[L_y, L_x] && (20\text{-}28)\\
&= -2i[L_x, L_y] && (20\text{-}29)\\
&= -2ii\hbar L_z && (20\text{-}30)\\
&= 2\hbar L_z && (20\text{-}31)
\end{aligned}$$

$$\boxed{[L_+, L_-] = 2\hbar L_z} \tag{20-32}$$

$$\begin{aligned}
[L_\pm, L_z] &= [L_x \pm iL_y, L_z] && (20\text{-}33)\\
&= [L_x, L_z] \pm i[L_y, L_z] && (20\text{-}34)\\
&= -i\hbar L_y \pm i(i\hbar L_x) && (20\text{-}35)\\
&= \mp\hbar L_x - i\hbar L_y && (20\text{-}36)\\
&= \mp\hbar(L_x \pm L_y) && (20\text{-}37)\\
&= \mp\hbar L_\pm && (20\text{-}38)
\end{aligned}$$

$$\boxed{[L_\pm, L_z] = \mp\hbar L_\pm} \tag{20-39}$$

We also note that

$$\begin{aligned}
L_+L_- &= (L_x + iL_y)(L_x - iL_y) && (20\text{-}40)\\
&= L_x^2 + L_y^2 - iL_xL_y + L_yL_x && (20\text{-}41)\\
&= L^2 - L_z^2 - i[L_x, L_y] && (20\text{-}42)\\
&= \mathbf{L}^2 - L_z^2 + \hbar L_z && (20\text{-}43)
\end{aligned}$$

and similarly $L_-L_+ = \mathbf{L}^2 - \mathbf{L}_z^2 - \hbar L_z$.

$$\boxed{\begin{aligned} L_+L_- &= \mathbf{L}^2 - \mathbf{L}_z^2 + \hbar L_z \\ L_-L_+ &= \mathbf{L}^2 - \mathbf{L}_z^2 - \hbar L_z \end{aligned}}$$

As for the HO, we now proceed to analyze the range of allowed values for l, m: Since $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$ and L_x, L_y, L_z are Hermitian operators, we have

$$\langle l,m|L_x^2|l,m\rangle = \langle L_x^\dagger(l,m)|L_x(l,m)\rangle = \langle L_x(l,m)|L_x(l,m)\rangle \geq 0, \tag{20-44}$$

similarly for y, z, and consequently $\langle l,m|\mathbf{L}^2|l,m\rangle \geq 0$ or

$$0 \leq \langle l,m|\mathbf{L}^2|l,m\rangle = \hbar^2 l(l+1)\langle l,m|l,m\rangle = \hbar^2 l(l+1). \tag{20-45}$$

Consequently, we can choose $l \geq 0$. (If $l \leq -1$, we define $l' := -(l+1)$, then $l(l+1) = -l'(l'+1)$ and $l' \geq 0$.) To understand the operators $L_\pm$, let us define a new state

$$|\psi_\pm\rangle := L_\pm|l,m\rangle, \tag{20-46}$$

and act on it with $\mathbf{L}^2$.

$$\begin{aligned} \mathbf{L}^2|\psi_\pm\rangle &= \mathbf{L}^2 L_\pm|l,m\rangle && (20\text{-}47)\\ &= L_\pm\mathbf{L}^2|l,m\rangle && (20\text{-}48)\\ &= \hbar^2 l(l+1)L_\pm|l,m\rangle && (20\text{-}49)\\ &= \hbar^2 l(l+1)|\psi_\pm\rangle, && (20\text{-}50) \end{aligned}$$

so $|\psi_\pm\rangle$ is an eigenstate of $\mathbf{L}^2$ with the same quantum number l. Also we have

$$\begin{aligned} L_z|\psi_\pm\rangle &= L_z L_\pm|l,m\rangle && (20\text{-}51)\\ &= (L_\pm L_z \pm \hbar L_\pm)|l,m\rangle && (20\text{-}52)\\ &= (m\hbar \pm \hbar)L_\pm|l,m\rangle && (20\text{-}53)\\ &= (m\pm 1)\hbar L_\pm|l,m\rangle && (20\text{-}54)\\ &= (m\pm 1)\hbar|\psi_\pm\rangle. && (20\text{-}55) \end{aligned}$$

This means that $L_\pm|l,m\rangle$ is also an eignenstate of L_z, but with an eigenvalue $(m\pm1)\hbar$ that differs from the original one by one. Since m is the quantum number associated with the z component of angular momentum, we call m **the azimuthal (or magnetic) quantum number**, while l **is the quantum number associated with total angular momentum**. L_+ (L_-) raises (lowers) the magnetic quantum number by one, while preserving the total angular momentum l.

Let us calculate the length of

$$|l,\widetilde{m\pm 1}\rangle := L_\pm|l,m\rangle, \tag{20-56}$$

the unnormalized state vector.

$$\langle l, \widetilde{m \pm 1} | l, \widetilde{m \pm 1} \rangle = \langle l, m | L_{\mp} L_{\pm} l, m \rangle \tag{20-57}$$

$$= \langle l, m | \mathbf{L}^2 - L_z^2 \mp \hbar L_z | l, m \rangle \tag{20-58}$$

$$= \hbar^2 l(l+1) - \hbar^2 m^2 \mp \hbar^2 m^2) \langle l, m | l, m \rangle \tag{20-59}$$

$$= \hbar^2 \big(l(l+1) - m(m \pm 1) \big) \tag{20-60}$$

$$= \hbar^2 (l \mp m)(l \pm m + 1) \tag{20-61}$$

Since the length squared of any vector must be non-negative, it follows that

$$l(l+1) - m(m \pm 1) \geq 0. \tag{20-62}$$

Consequently,

$$m(m \pm 1) = m^2 \pm m + \frac{1}{4} - \frac{1}{4} \tag{20-63}$$

$$= \left(m \pm \frac{1}{2} \right)^2 - \frac{1}{4} \tag{20-64}$$

$$\leq l^2 + l = \left(l + \frac{1}{2} \right)^2 - \frac{1}{4} \tag{20-65}$$

or

$$\left| m \pm \frac{1}{2} \right| \leq \left| +\frac{1}{2} \right| = l + \frac{1}{2} \tag{20-66}$$

since $l \geq 0$,

$$m \leq l, \text{ for } m > 0 \tag{20-67}$$

and also

$$-m \leq l, \text{ for } m \leq 0. \tag{20-68}$$

Therefore, m is bounded both from above and from below:

$$\boxed{-l \leq m \leq l}, \; l \geq 0. \tag{20-69}$$

Since $|\psi_+\rangle = L_+ |l, m\rangle$ is also an eigenstate of $\mathbf{L}^2$ and L_z, but with new eigenvalue $m' = m + 1$, the bound on m is only consistent with this fact if $L_+ |l, m\rangle = 0$ for some m. Consequently, with

$$L_+ |l, m\rangle = |l, \widetilde{m+1}\rangle \tag{20-70}$$

$$0 = \langle l, \widetilde{m+1} | l, \widetilde{m+1} \rangle \tag{20-71}$$

$$= \hbar^2 (l - m)(l + m + 1). \tag{20-72}$$

$$\boxed{m_{\max} = l} \tag{20-73}$$

Similarly, for
$ket\psi_- = L_-|l, m\rangle$ we have

$$\boxed{m_{\min} = -l}. \tag{20-74}$$

Thus, we have a ladder of eigenvalues spaced by one, and connected by the raising and lowering operators L_+ and L_-

$$\boxed{m = -l, -l+1, \ldots, l-1, l}, \; l \geq 0 \tag{20-75}$$

This is only possible is l is integer or half integer. It turns out that half-integer

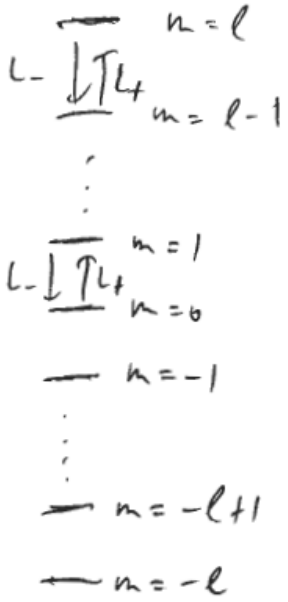

Figure I: Ladder of eigenvalues for fixed l.

values of l have no simple spatial representation, and correspond to an internal form of angular momentum called **spin** of the particle. Here we will restrict ourselves to **orbital angular momentum**, which requires l to be an **integer**.

Summary: angular momentum derivation

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{21-1}$$

$$L_x = yp_z - zp_y, \text{ etc.} \tag{21-2}$$

$$[x, p_y] = 0, \text{ etc.} \tag{21-3}$$

Angular momentum commutation relations

$$[L_x, L_y] = i\hbar L_z \tag{21-4}$$

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k \tag{21-5}$$

Levi-Civita symbol:

$$\epsilon_{ijk} = \begin{cases} +1 & \text{for even permutation of } xyz \\ -1 & \text{for odd permutation} \end{cases} \tag{21-6}$$

In general, no simultaneous eigenstates of L_x, L_y, L_z,

$$\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2, \tag{21-7}$$

$$[\mathbf{L}^2, L_x] = [\mathbf{L}^2, L_y] = [\mathbf{L}^2, L_z] = 0, \tag{21-8}$$

simultaneous eigenstates of $\mathbf{L}^2$ and one component (L_z).

Define, without loss of generality, simultaneous eigenstates $|l, m\rangle$ of $\mathbf{L}^2$ and L_z such that

$$L_z|l, m\rangle = m\hbar|l, m\rangle \quad \rightarrow \quad m \text{ magnetic quantum number} \tag{21-9}$$

$$\mathbf{L}^2|l, m\rangle = \hbar^2 l(l+1)|l, m\rangle \quad \rightarrow \quad \begin{pmatrix} l \geq 0 \text{ quantum number of} \\ \text{total average momentum} \end{pmatrix} \tag{21-10}$$

$$\langle l', m'|l, m\rangle = \delta_{ll'}\delta_{mm'}, \quad \rightarrow \quad \text{orthonormality} \tag{21-11}$$

Raising and lowering operators

$$L_\pm = L_x \pm iL_y = L_\pm^\dagger \tag{21-12}$$

$$[\mathbf{L}^2, L_\pm] = 0 \tag{21-13}$$

Note. $L_\pm$ preserves l.

$$L_\pm|l,m\rangle = |l,\widetilde{m\pm 1}\rangle, \text{ from } [L_\pm, L_z] = \mp\hbar L_\pm \tag{21-14}$$

Note. $L_\pm$ increases (lowers) magnetic quantum number by 1.

$$\langle l,\widetilde{m\pm 1}|l,\widetilde{m\pm 1}\rangle = \langle L_\pm l,m|L_\pm l,m\rangle = \hbar^2(l\mp m)(l\pm m+1) \tag{21-15}$$

$$\boxed{|m|\leq l} \tag{21-16}$$

Since L_+ increases m by 1 we need $L_+|l,m_{\max}\rangle = 0$ for some $m_{\max}$ or

$$\langle l,\widetilde{m_{\max}+1}|l,\widetilde{m_{\max}+1}\rangle = \hbar^2(l-m_{\max})(l+m_{\max}+1) = 0 \tag{21-17}$$

$$\boxed{m_{\max} = l} \tag{21-18}$$

$$L_-|l,m_{\min}\rangle = 0, \text{ for some } m_{\min} \tag{21-19}$$

$$\langle l,\widetilde{m_{\min}-1}|l,\widetilde{m_{\min}-1}\rangle = \hbar^2(l+m_{\min})(l-m_{\min}+1) = 0 \tag{21-20}$$

$$\boxed{m_{\min} = -l} \tag{21-21}$$

since $m_{\max} - m_{\min}$ = integer (integer number of application of L_+ onto $|l,m_{\min}\rangle$). We need $m_{\max} - m_{\min} = 2l$ = integer. (l integer of half-integer.)

Non-degenerate Perturbation Theory

$H = H_0 + H'$

$H' \ll H_0$

$H_0 \psi_n^0 = E_n^0 \psi_n^0$ has been solved.

$\{ \psi_n^0 , E_n^0 \}$

Non-degerenate

Corresponds to each E_n^0, there is one linear independent ψ_n^0

$\{ \psi_n^0 \}$ forms an orthonormal set, i.e.,

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm}$$

Want to solve

$$H \psi_n = E_n \psi_n$$

Usually, we cannot solve the equation exactly.

↓

approximate solution is sought

Perturbation theory is a systematic proceedure for obtaining approximate solutions

$$H = H_0 + \lambda H'$$

↓

keep track of the order of the approximation

in the end, will be set to be 1

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

E_n^1 → first-order correction to the nth eigenvalue

ψ_n^1 → first order correction to the nth eigenfunction

$$(H_0 + \lambda H')(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots)$$
$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots)$$

λ^0 $\quad H_0 \psi_n^0 = E_n^0 \psi_n^0$

↓ given starting point

λ^1 $\quad H_0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$

λ^2 $\quad H_0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$

⋮

First order perturbation

$$\langle \psi_n^0 | H_0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle + E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

$$\langle H_0 \psi_n^0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^1 + E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

$$E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

$$\Rightarrow \quad \underline{\underline{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle}}$$

$$(H_0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$$

$$\psi_n^1 = \sum_{m \neq n} C_m^{(n)} \psi_m^0$$

$$\sum_{m\neq n} (E_m^\circ - E_n^\circ) C_m^{(n)} \psi_m^\circ = -(H' - E_n') \psi_n^\circ$$

Taking the inner product with ψ_ℓ°

$$\sum_{m\neq n} (E_m^\circ - E_n^{(0)}) C_m^{(n)} \underbrace{\langle \psi_\ell^\circ | \psi_m^\circ \rangle}_{\delta_{\ell m}} = -\langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle + E_n' \langle \psi_\ell^\circ | \psi_n^\circ \rangle$$

If $\ell = n$, then $\ell = m$, LHS = 0, then

$$E_\ell' = \langle \psi_\ell^\circ | H' | \psi_\ell^\circ \rangle$$

↓ first order energy correction we obtained early.

If $\ell \neq n$

$$(E_\ell^\circ - E_n^\circ) C_\ell^{(n)} = -\langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle$$

$$\Rightarrow \quad C_m^{(n)} = \frac{\langle \psi_m^\circ | H' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ}$$

$$\Rightarrow \quad \psi_n' = \sum_{m\neq n} \frac{\langle \psi_m^\circ | H' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ} \psi_m^\circ$$

- The denominator is safe, since there is no coefficient $m = n$ as long as the unperturbed energy spectrum is non-degenerate.

If there is degeneracy, the procedure developed here is in trouble

↓ degenerate perturbation theory must be used. (we shall discuss this point lately).

Remarks:

- It is obvious that this procedure is valid for non-degenerate case
- ψ_n' is orthogonal to ψ_n°

Second order perturbation theory

$$H_\circ \psi_n^2 + H' \psi_n' = E_n^\circ \psi_n^2 + E_n' \psi_n' + E_n^2 \psi_n^\circ$$

$$\Rightarrow \quad (H_\circ - E_n^\circ)\psi_n^2 = E_n' \psi_n' + E_n^2 \psi_n^\circ - H' \psi_n' \quad (1)$$

$$\langle \psi_n^\circ | (H_\circ - E_n^\circ) | \psi_n^2 \rangle = E_n' \langle \psi_n^\circ | \psi_n' \rangle + E_n^2 - \langle \psi_n^\circ | H' | \psi_n' \rangle$$

$$\| \quad (E_n^{(0)} - E_n^\circ) \langle \psi_n^\circ | \psi_n^2 \rangle$$

$$\| \quad 0$$

$$\Rightarrow \quad E_n^2 = \langle \psi_n^\circ | H' | \psi_n' \rangle$$

$$= \langle \psi_n^\circ | H' | \sum_{m \neq n} \frac{\langle \psi_m^\circ | H' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ} \psi_m^\circ \rangle$$

$$= \sum_{m \neq n} \frac{1}{E_n^\circ - E_m^\circ} \langle \psi_n^\circ | H' | \psi_m^\circ \rangle \langle \psi_m^\circ | H' | \psi_n^\circ \rangle$$

$$= \sum_{m \neq n} \frac{|\langle \psi_n^\circ | H' | \psi_m^\circ \rangle|^2}{E_n^\circ - E_m^\circ}$$

Remarks

(i) $E_n^{(1)}$, $E_n^{(2)}$ are real as it should be

(ii) If ψ_n is the ground state, i.e, the state of lowest energy, then $E_n^{(0)} < E_k^{(0)}$ for all $k \Rightarrow E_n^{(2)}$ is negative

(iii) All other things being equal, if all the matrix elements of V are of roughly the same order of magnitude, then nearby levels have a bigger effect on the second order energy shift than distance ones.

(iv) If an important level "k" lies above level "n" then the second order term tends to bring the energy of nth state downward. If an important level "k" lies below level "n" then the second order term tends to bring the energy of nth state upward.

Example

Anharmonic Perturbation

$H_0 = \frac{p^2}{2m} + \frac{1}{2}kx^2$ one-dimensional harmonic oscillator

$V = ax^3 + bx^4$

$E_n^{(0)} = (n+\frac{1}{2})\hbar\omega, \quad \{\psi_n^{(0)}\}$

$\int \psi_n^{(0)*} \psi_m^{(0)} d^3x = \delta_{nm}$

$R_+ \psi_n^0 = \sqrt{n+1}\, \psi_{n+1}^0$

$R_- \psi_n^0 = \sqrt{n}\, \psi_{n-1}^0$

$x = \sqrt{\frac{\hbar}{2m\omega}} (R_+ + R_-)$

It can be shown that

$(R_+ + R_-)\psi_n^0 = \sqrt{n+1}\, \psi_{n+1}^0 + \sqrt{n}\, \psi_{n-1}^0$

$(R_+ + R_-)^2 \psi_n^0 = \sqrt{n(n-1)}\, \psi_{n-2}^0 + (2n+1)\psi_n^0 + \sqrt{(n+1)(n+2)}\, \psi_{n+2}^0$

$(R_+ + R_-)^3 \psi_n^0 = \sqrt{n(n-1)(n-2)}\, \psi_{n-3}^0 + 3n\sqrt{n}\, \psi_{n-1}^0 + (3n+3)\sqrt{n+1}\, \psi_{n+1}^0 + \sqrt{(n+1)(n+2)(n+3)}\, \psi_{n+3}^0$

$(R_+ + R_-)^4 \psi_n^0 = \sqrt{n(n-1)(n-2)(n-3)}\, \psi_{n-4}^0 + \sqrt{n(n-1)}\,(4n-2)\psi_{n-2}^0 + \sqrt{n(n+1)}\,(4n+6)\psi_{n+2}^0$

$+ \sqrt{(n+1)(n+2)(n+3)(n+4)}\, \psi_{n+4}^0 + \{(3n+3)(n+1) + 3n\cdot n\}\psi_n^0$

$V_{nn} = \int \psi_n^{(0)*} V \psi_n^0 d^3x = \langle \psi_n^0 | H' | \psi_n^0 \rangle$

It is obvious that ax^3 term gives no contribution

$V_{nn} = b\frac{\hbar^2}{4m^2\omega^2}[(3n+3)(n+1) + 3n\cdot n] = \frac{3b\hbar^2}{4m^2\omega^2}(2n^2+2n+1)$

To calculate $\psi_n^{(1)}$, $E_n^{(2)}$, all we have to know is V_{kn} which can be easily read off from above relations

Note: V_{kn} is non-zero only if $k = n-4, n-3, \cdots n+4$

$\Rightarrow$ the series for $\psi_n^{(1)}$, $E_n^{(2)}$ contains only a few terms

Degenerate Perturbation Theory

Unperturbed states are degenerate

↓

Two (or more) distinct states share the same energy

Use twofold degeneracy as example

↓

generalize to N-fold degeneracy

$$H^\circ \psi_a^\circ = E^\circ \psi_a^\circ, \quad H^\circ \psi_b^\circ = E^\circ \psi_b^\circ$$

and

$$\langle \psi_a^\circ | \psi_b^\circ \rangle = 0$$

Any linear combination of these states

$$\psi^\circ = \alpha \psi_a^\circ + \beta \psi_b^\circ$$

still an eigenstate of H° with the same eigenvalue E°

$$H^\circ \psi^\circ = E^\circ \psi^\circ$$

$$H\psi = E\psi \qquad H = H^\circ + \lambda H'$$

$$E^\circ = E^\circ + \lambda E' + \lambda^2 E^2 + \cdots$$

$$\psi = \psi^\circ + \lambda \psi' + \lambda^2 \psi^2 + \cdots$$

$$H^\circ \psi^\circ + \lambda (H'\psi^\circ + H^\circ \psi') + \cdots$$

$$= E^\circ \psi^\circ + \lambda (E' \psi^\circ + E^\circ \psi') + \cdots$$

$$H^\circ \psi' + H'\psi^\circ = E^\circ \psi' + E' \psi^\circ \quad \leftarrow \text{first order in } \lambda$$

$\langle \psi_a^\circ | \check{H}^\circ \psi' \rangle + \langle \psi_a^\circ | H' \psi^\circ \rangle$ inner product with ψ_a°

$= E^\circ \langle \psi_a^\circ | \psi' \rangle + E' \langle \psi_a^\circ | \psi^\circ \rangle$

$\check{}$ cancels

$$\alpha \langle \psi_a^\circ | H' | \psi_a^\circ \rangle + \beta \langle \psi_a^\circ | H' | \psi_b \rangle = \alpha E'$$

Define $W_{ij} = \langle \psi_i^\circ | H' | \psi_j \rangle \quad (i, j = a, b)$

$$\Rightarrow \quad \alpha W_{aa} + \beta W_{ab} = \alpha E' \qquad (A)$$

Take inner product with ψ_b°

$$\Rightarrow \quad \alpha W_{ba} + \beta W_{bb} = \beta E' \qquad (B)$$

Eliminate β from (A) and (B)

$$\Rightarrow \quad \alpha [W_{ab} W_{ba} - (E' - W_{aa})(E' - W_{bb})] = 0$$

If $\alpha \neq 0$

$$(E')^2 - E' (W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} W_{ba}) = 0$$

$$E'_\pm = \frac{1}{2} [W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4 |W_{ab}|^2} \qquad (C)$$

With E'_+ given, (A), (B) + $\alpha^2 + \beta^2 = 1$

$$\Rightarrow \quad \alpha_+, \beta_+ \quad \Rightarrow \quad \psi_+^\circ = \alpha_+ \psi_a^\circ + \beta_+ \psi_b^\circ$$

With E'_- given $\Rightarrow \alpha_-, \beta_-$

$$\Rightarrow \quad \psi_-^\circ = \alpha_- \psi_a^\circ + \beta_- \psi_b^\circ$$

This is the fundamental result of degenerate perturbation.

If $\alpha = 0 \Rightarrow$ (A) implies $W_{ab} = 0 \Rightarrow E' = W_{bb}$

$E_+^1 = W_{bb} = \langle \psi_b^0 | H' | \psi_b^0 \rangle$

$E_-^1 = W_{aa} = \langle \psi_a^0 | H' | \psi_a^0 \rangle$

$\Rightarrow$ $|\psi_a^0\rangle$, $|\psi_b^0\rangle$ are the "good" states right from the states right from the start

↓

condition $W_{ab} = 0$

Theorem Let A be a Hermitian operator that commutes with H'. If ψ_a^0 and ψ_b^0 are eigenfunctions of A with distinct eigenvalues

$A\psi_a^0 = \mu\psi_a^0$, $A\psi_b^0 = \nu\psi_b^0$ and $\mu \neq \nu$

then $W_{ab} = 0$ (and hence ψ_a^0 and ψ_b^0 are the "good" states to use in perturbation theory

Proof $[A, H'] = 0$

$\langle \psi_a^0 | [A, H'] \psi_b^0 \rangle = 0$

$= \langle \psi_a^0 | AH' \psi_b^0 \rangle - \langle \psi_a^0 | H'A \psi_b^0 \rangle$

$= \langle A\psi_a^0 | H' \psi_b^0 \rangle - \langle \psi_a^0 | H' \nu \psi_b^0 \rangle$

$= (\mu - \nu) \langle \psi_a^0 | H' | \psi_b^0 \rangle = (\mu - \nu) W_{ab}$

$\mu \neq \nu \quad \Rightarrow \quad W_{ab} = 0$

Faced degenerate states, look around for some Hermitian operator A that commutes with H'; pick as your unperturbed states that are simultaneous eigenfunction of H^0 and A. Then use ordinary first order perturbation theory

If you can't find such as operator, you will have to use (C)

Example: spin-orbit interaction

$$H' = \frac{1}{2m^2c^2}\frac{Ze^2}{r^3}\vec{S}\cdot\vec{L}$$

A: L^2, J^2, S^2, J_z

$$E'_{n,l,s,j,m_j} = \langle n,l,s,j,m_j | H' | n,l,s,j,m_j \rangle$$

↓

go back to P. 11-4 and Chapter 9

Example Stark Effect in Hydrogen Atom (for $n=2$ Level.

$V = eEz$, we have taken $\vec{E}$ to be parallel to z direction.

Unperturbed Hamiltonian has 4-fold degeneracy

$\psi_{200} \rightarrow \psi_{2s}$ $\quad n=2,\ l=0,\ m=0$

$\psi_{211} \rightarrow \psi_{2P_1}$ $\quad n=2,\ l=1,\ m=1$

$\psi_{210} \rightarrow \psi_{2P_0}$ $\quad n=2,\ l=1,\ m=0$

$\psi_{21-1} \rightarrow \psi_{2P_{-1}}$ $\quad n=2,\ l=1,\ m=-1$

All have the same unperturbed energy $E_2^{(0)} = -\frac{me^4}{2\hbar^2}\cdot\frac{1}{4}$

Note $[L_z, H] = 0$ because $[L_z, H_0] = 0$ and $[L_z, z] = 0$

$\leftrightarrow [L_z, V] = 0$ $\quad [H, L_x] \neq 0,\ [H, L_y] \neq 0$

$\Rightarrow$ L_z is constant of motion

$\Rightarrow$ Perturbation only mixes $\psi^{(0)}_{200}$ and $\psi^{(0)}_{210}$; will not mix $\psi^{(0)}_{211}$ and $\psi^{(0)}_{21-1}$ with other states.

$$\int \psi_{211}^{(0)*} V \psi_{21-1}^{(0)} d^3x = 0$$

Proof: $L_z V \psi_{21-1}^{(0)} = V L_z \psi_{21-1}^{(0)} = V(-1)\psi_{21-1}^{(0)} = -V\psi_{21-1}^{(0)}$

$\Rightarrow$ $V\psi_{21-1}^{(0)}$ is an eigenfunction of L_z with eigenvalue -1

$\psi_{211}^{(0)}$ is an eigenvalue of L_z with eigenvalue $+1$

$\Rightarrow$ $\psi_{211}^{(0)}$ and $V\psi_{21-1}^{(0)}$ is orthogonal $\Rightarrow$ thus the proof.

Similarily, $\int \psi_{211}^{(0)} V \psi_{210} d^3x = \int \psi_{211}^{(0)} V \psi_{200} d^3x = 0$

$\Rightarrow$ States with different m will not mix

	$\ell=1$ $m=1$	$\ell=1$ $m=0$	$\ell=1$ $m=-1$	$\ell=0$ $m=0$
$\ell=1, m=1$	x	0	0	0
$\ell=1, m=0$	0	x	0	x
$\ell=1, m=-1$	0	0	x	0
$\ell=0, m=0$	0	x	0	x

$\psi_{21-1}^{(0)}$, $\psi_{21-1}^{(0)}$ clearly are already the eigenfunction of the V matrix

$$E_{2,1,1}^{(1)} = \int \psi_{2,1,1}^{(0)*} V \psi_{2,1,1}^{(0)} d^3x$$

$= 0$ from parity consideration

$E_{2,1,-1}^{(1)}$ also equal to zero

$\Rightarrow$ In first order perturbation, the energies for $(2,1,1)$, $(2,1,-1)$ is unchanged

There is mixing between $\psi_{210}^{(0)}$ and $\psi_{200}^{(0)}$

$\Rightarrow$ degenerate perturbation method has to be used.

$n_1 \rightarrow (2,0,0)$, $n_2 \rightarrow (2,1,0)$

$V_{11} = \int \psi_{200}^{(0)*} eEz \, \psi_{200}^{(0)} d^3x = 0$ from parity consideration.

$V_{22} = \int \psi_{210}^{(0)*} eEz \, \psi_{210}^{(0)} d^3x = 0$ from parity consideration.

$V_{12} = \int \psi_{200}^{*} eEz \, \psi_{210}^{(0)} d^3x$

$= \left[\int \psi_{210}^{(0)*} eEz \, \psi_{200} d^3x \right]^*$

$= V_{21}^*$

$V_{12} = \int \frac{1}{\sqrt{32\pi a^3}} \left(2 - \frac{r}{a}\right) e^{-r/2a} eEr\cos\theta \frac{1}{\sqrt{32\pi a^3}} \frac{r}{a} e^{-r/a} \cos\theta \cdot r^2 dr \, d(\cos\theta) \, d\phi$

a = Bohr radius

Carry out the integration

$V_{12} = -3eEa$

The eigenvalue equation to be solved is

$$\begin{pmatrix} 0 & -3eEa \\ -3eEa & 0 \end{pmatrix} \begin{pmatrix} C_{11} \\ C_{21} \end{pmatrix} = E_{n_1}^{(1)} \begin{pmatrix} C_{11} \\ C_{21} \end{pmatrix}$$

$$\begin{pmatrix} 0 & -3eEa \\ -3eEa & 0 \end{pmatrix} \begin{pmatrix} C_{12} \\ C_{22} \end{pmatrix} = E_{n_2}^{(1)} \begin{pmatrix} C_{12} \\ C_{22} \end{pmatrix}$$

The solutions are

$E_{n_1}^{(1)} = 3eEa \qquad C_{11} = C_{21} = \frac{1}{\sqrt{2}}$ (we have normalized the wave function)

$E_{n_2}^{(2)} = -3eEa \qquad C_{12} = -C_{22} = \frac{1}{\sqrt{2}}$

Summary

Wave Function (Zeroth Order)	Energ Level to First Order
$\psi_{211}^{(0)}$	$-\frac{me^4}{2\hbar^2} \cdot \frac{1}{4}$
$\psi_{21-1}^{(0)}$	$-\frac{me^4}{2\hbar^2} \cdot \frac{1}{4}$
$\frac{1}{\sqrt{2}}(\psi_{200}^{(0)} + \psi_{210}^{(0)})$	$-\frac{me^4}{2\hbar^2} \cdot \frac{1}{4} + 3eEa$
$\frac{1}{\sqrt{2}}(\psi_{200}^{(0)} - \psi_{210}^{(0)})$	$-\frac{me^4}{2\hbar^2} \cdot \frac{1}{4} - 3eEa$

Time-Dependent Perturbation Theory

We consider here only those phenomena that are described by Hamiltonians which can be split into two parts, a time-independent part $\hat{H}_0$ and a time-dependent part $\hat{V}(t)$ that is small compared to $\hat{H}_0$:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t), \tag{10.22}$$

where $\hat{H}_0$, which describes the system when unperturbed, is assumed to have exact solutions that are known. Such splitting of the Hamiltonian is encountered in the following typical problem. Consider a system which, when unperturbed, is described by a time-independent Hamiltonian $\hat{H}_0$ whose solutions—the eigenvalues E_n and eigenstates, $\mid \psi_n\rangle$—are known,

$$\hat{H}_0 \mid \psi_n\rangle = E_n \mid \psi_n\rangle, \tag{10.23}$$

and whose most general state vectors are given by stationary states

$$\mid \Psi_n(t)\rangle = e^{-i\hat{H}_0 t/\hbar} \mid \psi_n\rangle = e^{-iE_n t/\hbar} \mid \psi_n\rangle. \tag{10.24}$$

In the time interval $0 \leq t \leq \tau$ we subject the system to an external time-dependent perturbation, $\hat{V}(t)$, that is small compared to $\hat{H}_0$:

$$\hat{V}(t) = \begin{cases} \hat{V}(t) & 0 \leq t \leq \tau \\ 0 & t < 0, \quad t > \tau. \end{cases} \tag{10.25}$$

During the time interval $0 \leq t \leq \tau$, the Hamiltonian of the system is $\hat{H} = \hat{H}_0 + \hat{V}(t)$, and the corresponding Schrödinger equation is

$$i\hbar \frac{d \mid \Psi(t)\rangle}{dt} = (\hat{H}_0 + \hat{V}(t)) \mid \Psi(t)\rangle. \tag{10.26}$$

where $\hat{V}(t)$ characterizes the interaction of the system with the external source of perturbation.

How does $\hat{V}(t)$ affect the system? When the system interacts with $\hat{V}(t)$, it either absorbs or emits energy. This process inevitably causes the system to undergo transitions from one unperturbed eigenstate to another. The main task of time-dependent perturbation theory consists of answering this question: If the system is initially in an (unperturbed) eigenstate $\mid \psi_i\rangle$ of $\hat{H}_0$, what is the probability that the system will be found at a later time in another unperturbed eigenstate $\mid \psi_f\rangle$?

To prepare the ground for answering this question, we need to look for the solutions of the Schrödinger equation (10.26). The standard method to solve (10.26) is to expand $\mid \Psi(t)\rangle$ in terms of an expansion coefficient $c_n(t)$:

$$\mid \Psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t} \mid \psi_n\rangle, \tag{10.27}$$

and then insert this into (10.26) to find $c_n(t)$ to various orders in the approximation. Instead of following this procedure, and since we are dealing with time-dependent potentials, it is more convenient to solve (10.26) in the interaction picture (10.19):

$$i\hbar \frac{d \mid \Psi(t)\rangle_I}{dt} = \hat{V}_I(t) \mid \Psi(t)\rangle_I, \tag{10.28}$$

where $\mid \Psi(t)\rangle_I = e^{iH_0 t/\hbar} \mid \Psi(t)\rangle$ and $\hat{V}_I(t) = e^{iH_0 t/\hbar} \hat{V}(t) e^{-iH_0 t/\hbar}$. The time evolution equation $\mid \Psi(t)\rangle = \hat{U}(t, t_i) \mid \Psi(t_i)\rangle$ may be written in the interaction picture as

$$\mid \Psi(t)\rangle_I = e^{i\hat{H}_0 t/\hbar} \mid \Psi(t)\rangle = e^{i\hat{H}_0 t/\hbar} \hat{U}(t, t_i) \mid \Psi(t_i)\rangle = e^{i\hat{H}_0 t/\hbar} \hat{U}(t, t_i) e^{-i\hat{H}_0 t_i/\hbar} \mid \Psi(t_i)\rangle_I, \tag{10.29}$$

or as

$$\mid \Psi(t)\rangle_I = \hat{U}_I(t, t_i) \mid \Psi(t_i)\rangle_I, \tag{10.30}$$

where the time evolution operator is given in the interaction picture by

$$\hat{U}_I(t,t_i) = e^{i\hat{H}_0 t/\hbar}\hat{U}(t,t_i)e^{-i\hat{H}_0 t_i/\hbar}. \tag{10.31}$$

Inserting (10.30) into (10.28) we end up with

$$i\hbar\frac{d\hat{U}_I(t,t_i)}{dt} = \hat{V}_I(t)\hat{U}_I(t,t_i). \tag{10.32}$$

The solutions of this equation, with the initial condition $\hat{U}_I(t_i,t_i) = \hat{I}$, are given by the *integral equation*

$$\hat{U}_I(t,t_i) = 1 - \frac{i}{\hbar}\int_{t_i}^{t}\hat{V}_I(t')\hat{U}_I(t',t_i)\,dt'. \tag{10.33}$$

Time-dependent perturbation theory provides *approximate* solutions to this integral equation. This consists in assuming that $\hat{V}_I(t)$ is *small then proceeding iteratively*. The first-order approximation is obtained by inserting $\hat{U}_I(t',t_i) = 1$ in the integral sign of (10.33), leading to $\hat{U}_I^{(1)}(t,t_i) = 1 - (i/\hbar)\int_{t_i}^{t}\hat{V}_I(t')\,dt'$. Substituting $\hat{U}_I(t',t_i) = \hat{U}_I^{(1)}(t',t_i)$ in the integral sign of (10.33) we get the second-order approximation:

$$\hat{U}_I^{(2)}(t,t_i) = 1 - \frac{i}{\hbar}\int_{t_i}^{t}\hat{V}_I(t')\,dt' + \left(-\frac{i}{\hbar}\right)^2\int_{t_i}^{t}\hat{V}_I(t_1)\,dt_1\int_{t_i}^{t_1}\hat{V}_I(t_2)\,dt_2. \tag{10.34}$$

The third-order approximation is obtained by substituting $\hat{U}_I^{(2)}(t,t_i)$ into (10.33), and so on. A repetition of this iterative process yields

$$\begin{aligned}\hat{U}_I(t,t_i) = 1 &- \frac{i}{\hbar}\int_{t_i}^{t}\hat{V}_I(t')dt' + \left(-\frac{i}{\hbar}\right)^2\int_{t_i}^{t}\hat{V}_I(t_1)dt_1\int_{t_i}^{t_1}\hat{V}_I(t_2)dt_2 + \cdots \\ &+ \left(-\frac{i}{\hbar}\right)^n\int_{t_i}^{t}\hat{V}_I(t_1)dt_1\int_{t_i}^{t_1}\hat{V}_I(t_2)dt_2\int_{t_i}^{t_2}\hat{V}_I(t_3)dt_3\cdots\int_{t_i}^{t_{n-1}}\hat{V}_I(t_n)dt_n + \cdots.\end{aligned} \tag{10.35}$$

This series, known as the *Dyson series*, allows for the calculation of the state vector up to the desired order in the perturbation.

We are now equipped to calculate the transition probability. It may be obtained by taking the matrix elements of (10.35) between the eigenstates of $\hat{H}_0$. Time-dependent perturbation theory, where one assumes knowledge of the solutions of the unperturbed eigenvalue problem (10.23), deals in essence with the calculation of the transition probabilities between the unperturbed eigenstates $|\,\psi_n\rangle$ of the system.

10.3.1 Transition Probability

The transition probability corresponding to a transition from an initial unperturbed state $|\,\psi_i\rangle$ to another unperturbed state $|\,\psi_f\rangle$ is obtained from (10.35):

$$\begin{aligned}P_{if}(t) = \left|\langle\psi_f\,|\,\hat{U}_I(t,t_i)\,|\,\psi_i\rangle\right|^2 = \Bigg|\langle\psi_f\,|\,\psi_i\rangle - \frac{i}{\hbar}\int_0^t e^{i\omega_{fi}t'}\langle\psi_f\,|\,\hat{V}(t')\,|\,\psi_i\rangle\,dt' \\ + \left(-\frac{i}{\hbar}\right)^2\sum_n\int_0^t e^{i\omega_{fn}t_1}\langle\psi_f\,|\,\hat{V}(t_1)\,|\,\psi_n\rangle\,dt_1\int_0^{t_1}e^{i\omega_{ni}t_2}\langle\psi_n\,|\,\hat{V}(t_2)\,|\,\psi_i\rangle\,dt_2 + \cdots\Bigg|^2,\end{aligned} \tag{10.36}$$

where we have used the fact that

$$\langle \psi_f \mid \hat{V}_I(t') \mid \psi_i \rangle = \langle \psi_f \mid e^{iH_0 t'/\hbar} \hat{V}(t') e^{-iH_0 t'/\hbar} \mid \psi_i \rangle = \langle \psi_f \mid V(t') \mid \psi_i \rangle \exp\left(i\omega_{fi} t'\right), \tag{10.37}$$

where ω_{fi} is the transition frequency between the initial and final levels i and f

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} = \frac{1}{\hbar}\left(\langle \psi_f \mid \hat{H}_0 \mid \psi_f \rangle - \langle \psi_i \mid \hat{H}_0 \mid \psi_i \rangle\right). \tag{10.38}$$

The transition probability (10.36) can be written in terms of the expansion coefficients $c_n(t)$ introduced in (10.27) as

$$P_{if}(t) = \left| c_f^{(0)} + c_f^{(1)}(t) + c_f^{(2)}(t) + \cdots \right|^2, \tag{10.39}$$

where

$$c_f^{(0)} = \langle \psi_f \mid \psi_i \rangle = \delta_{f,i}, \qquad c_f^{(1)}(t) = -\frac{i}{\hbar}\int_0^t \langle \psi_f \mid \hat{V}(t') \mid \psi_i \rangle e^{i\omega_{fi}t'} dt', \ldots. \tag{10.40}$$

The first-order transition probability for $\mid \psi_i \rangle \rightarrow \mid \psi_f \rangle$ with $i \neq f$ (and hence $\langle \psi_f \mid \psi_i \rangle = 0$) is obtained by terminating (10.36) at the first order in $V_I(t)$:

$$\boxed{P_{if}(t) = \left| -\frac{i}{\hbar}\int_0^t \langle \psi_f \mid \hat{V}(t') \mid \psi_i \rangle e^{i\omega_{fi}t'} dt' \right|^2}. \tag{10.41}$$

In principle we can use (10.36) to calculate the transition probability to any order in $\hat{V}_I(t)$. However, terms higher than the first order become rapidly intractable. For most problems of atomic and nuclear physics, the first order (10.41) is usually sufficient. In what follows, we are going to apply (10.41) to calculate the transition probability for two cases, which will have later usefulness when we deal with the interaction of atoms with radiation: a *constant* perturbation and a *harmonic* perturbation.

10.3.2 Transition Probability for a Constant Perturbation

In the case where $\hat{V}$ does not depend on time, (10.41) leads to

$$P_{if}(t) = \frac{1}{\hbar^2}\left| \langle \psi_f \mid \hat{V} \mid \psi_i \rangle \int_0^t e^{i\omega_{fi}t'} dt' \right|^2 = \frac{1}{\hbar^2}\left| \langle \psi_f \mid \hat{V} \mid \psi_i \rangle \right|^2 \left| \frac{e^{i\omega_{fi}t} - 1}{\omega_{fi}} \right|^2, \tag{10.42}$$

which, using $|e^{i\theta} - 1|^2 = 4\sin^2(\theta/2)$, reduces to

$$\boxed{P_{if}(t) = \frac{4|\langle \psi_f \mid \hat{V} \mid \psi_i \rangle|^2}{\hbar^2 \omega_{fi}^2} \sin^2\left(\frac{\omega_{fi}t}{2}\right)}. \tag{10.43}$$

As a function of time, this transition probability is an oscillating sinusoidal function with a period of $2\pi/\omega_{fi}$. As a function of ω_{fi}, however, the transition probability, as shown in Figure 10.1, has an interference pattern: it is appreciable only near $\omega_{fi} \simeq 0$ and decays rapidly as ω_{fi} moves away from zero (here, for a fixed t, we have assumed that ω_{fi} is a continuous

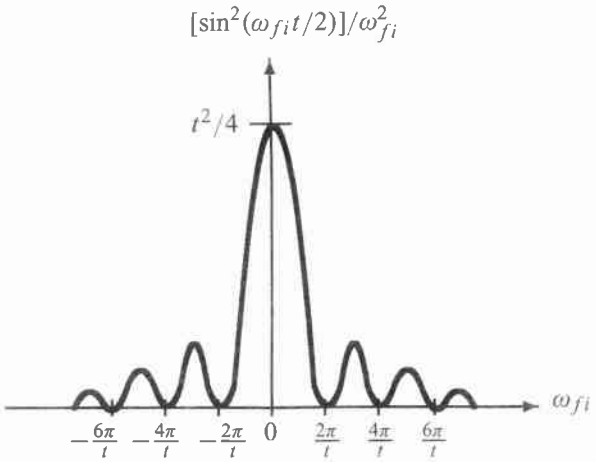

Figure 10.1 Plot of $[\sin^2(\omega_{fi}t/2)]/\omega_{fi}^2$ versus ω_{fi} for a fixed value of t; $\omega_{fi} = (E_f - E_i)/2$.

variable; that is, we have considered a continuum of final states; we will deal with this in more details in a moment). This means that the transition probability of finding the system in a state $|\psi_f\rangle$ of energy E_f is greatest only when $E_i \simeq E_f$ or when $\omega_{fi} \simeq 0$. The height and the width of the main peak, centered around $\omega_{fi} = 0$, are proportional to t^2 and $1/t$, respectively, so the area under the curve is proportional to t; since most of the area is under the central peak, the transition probability is proportional to t. The transition probability therefore grows linearly with time. The central peak becomes narrower and higher as time increases; this is exactly the property of a delta function. Thus, in the limit $t \to \infty$ the transition probability takes the shape of a delta function as we are going to see.

As $t \to \infty$ we can use the asymptotic relation (Appendix A)

$$\lim_{t\to\infty} \frac{\sin^2(yt)}{\pi y^2 t} = \delta(y) \tag{10.44}$$

to write the following expression:

$$\frac{1}{(\frac{1}{2}\omega_{fi})^2} \sin^2\left(\frac{\omega_{fi}t}{2}\right) = 2\pi t\hbar\delta(\hbar\omega_{fi}), \tag{10.45}$$

because $\delta(\omega_{fi}/2) = 2\hbar\delta(\hbar\omega_{fi})$. Now since $\hbar\omega_{fi} = E_f - E_i$, hence $\delta(\hbar\omega_{fi}) = \delta(E_f - E_i)$, we can reduce (10.43) in the limit of long times to

$$\boxed{P_{if}(t) = \frac{2\pi t}{\hbar} \left| \langle \psi_f \mid \hat{V} \mid \psi_i \rangle \right|^2 \delta(E_f - E_i).} \tag{10.46}$$

The *transition rate*, which is defined as a transition probability per unit time, is thus given by

$$\boxed{\Gamma_{if} = \frac{P_{if}(t)}{t} = \frac{2\pi}{\hbar} \left| \langle \psi_f \mid \hat{V} \mid \psi_i \rangle \right|^2 \delta(E_f - E_i).} \tag{10.47}$$

The delta term $\delta(E_f - E_i)$ guarantees the conservation of energy: in the limit $t \to \infty$, the transition rate is nonvanishing only between states of equal energy. Hence a constant (time

independent) perturbation neither removes energy from the system nor supplies energy to it. It simply causes energy-conserving transitions.

Transition into a continuum of final states

Let us now calculate the total transition rate associated with a transition from an initial state $|\psi_i\rangle$ into a continuum[1] of final states $|\psi_f\rangle$. If $\rho(E_f)$ is the density of final states—the number of states per unit energy interval—the number of final states within the energy interval E_f and $E_f + dE_f$ is equal to $\rho(E_f)\,dE_f$. The total transition rate W_{if} can then be obtained from (10.47):

$$W_{if} = \int \frac{P_{if}(t)}{t}\rho(E_f)\,dE_f = \frac{2\pi}{\hbar}|\langle\psi_f|\hat{V}|\psi_i\rangle|^2 \int \rho(E_f)\delta(E_f - E_i)\,dE_f, \quad (10.48)$$

or

$$\boxed{W_{if} = \frac{2\pi}{\hbar}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 \rho(E_i).} \quad (10.49)$$

This relation is called the *Fermi golden rule*. It implies that, in the case of a constant perturbation, if we wait long enough, the total transition rate becomes constant (time independent).

10.3.3 Transition Probability for a Harmonic Perturbation

Consider now a perturbation which depends harmonically on time (i.e., the time between the moments of turning the perturbation on and off):

$$\hat{V}(t) = \hat{v}e^{i\omega t} + \hat{v}^\dagger e^{-i\omega t}, \quad (10.50)$$

where $\hat{v}$ is a time-independent operator. Such a perturbation is encountered, for instance, when charged particles (e.g., electrons) interact with an electromagnetic field. This perturbation provokes transitions of the system from a stationary state to another.

The transition probability corresponding to this perturbation can be obtained from (10.41):

$$P_{if}(t) = \frac{1}{\hbar^2}\left|\langle\psi_f|\hat{v}|\psi_i\rangle\int_0^t e^{i(\omega_{fi}+\omega)t'}dt' + \langle\psi_f|\hat{v}^\dagger|\psi_i\rangle\int_0^t e^{i(\omega_{fi}-\omega)t'}dt'\right|^2. \quad (10.51)$$

Neglecting the cross terms, for they are negligible compared with the other two (because they induce no lasting transitions), we can rewrite this expression as

$$P_{if}(t) = \frac{1}{\hbar^2}\left|\langle\psi_f|\hat{v}|\psi_i\rangle\right|^2\left|\frac{e^{i(\omega_{fi}+\omega)t}-1}{\omega_{fi}+\omega}\right|^2 + \frac{1}{\hbar^2}\left|\langle\psi_f|\hat{v}^\dagger|\psi_i\rangle\right|^2\left|\frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega}\right|^2, \quad (10.52)$$

which, using $|e^{i\theta}-1|^2 = 4\sin^2(\theta/2)$, reduces to

$$P_{if}(t) = \frac{4}{\hbar^2}\left[\left|\langle\psi_f|\hat{v}|\psi_i\rangle\right|^2\frac{\sin^2((\omega_{fi}+\omega)t/2)}{(\omega_{fi}+\omega)^2} + \left|\langle\psi_f|\hat{v}^\dagger|\psi_i\rangle\right|^2\frac{\sin^2((\omega_{fi}-\omega)t/2)}{(\omega_{fi}-\omega)^2}\right]. \quad (10.53)$$

As displayed in Figure 10.2, the transition probability peaks either at $\omega_{fi} = -\omega$, where its maximum value is $P_{if}(t) = (t^2/4\hbar^2)|\langle\psi_f|\hat{v}|\psi_i\rangle|^2$, or at $\omega_{fi} = \omega$, where its maximum

[1] F. Schwabl, *Quantum Mechanics*, 2nd ed., Springer–Verlag, Berlin, 1995, Section 16.3.3.

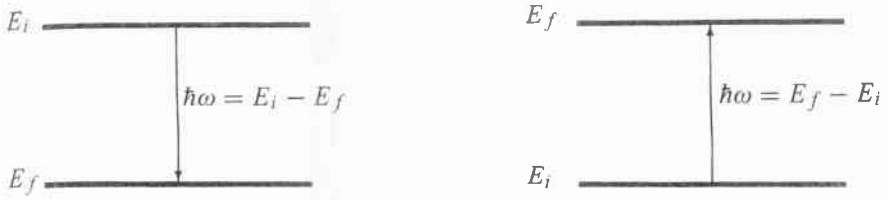

Figure 10.3 Stimulated emission and absorption of a photon of energy $\hbar\omega$.

Remark

For transitions into a continuum of final states, we can show, by analogy with the derivation of (10.49), that (10.54) leads to the absorption and emission transition rates:

$$W_{if}^{abs} = \frac{2\pi}{\hbar} \left| \langle \psi_f \mid \hat{V}^\dagger \mid \psi_i \rangle \right|^2 \rho(E_f)\Big|_{E_f = E_i + \hbar\omega}, \tag{10.57}$$

$$W_{if}^{emi} = \frac{2\pi}{\hbar} \left| \langle \psi_f \mid \hat{V} \mid \psi_i \rangle \right|^2 \rho(E_f)\Big|_{E_f = E_i - \hbar\omega}. \tag{10.58}$$

Since the perturbation (10.50) is Hermitian, $\langle \psi_f \mid \hat{v} \mid \psi_i \rangle = \langle \psi_i | \hat{v}^\dagger \mid \psi_f \rangle^*$, we have $|\langle \psi_f \mid \hat{v} \mid \psi_i \rangle|^2 = |\langle \psi_f \mid \hat{v}^\dagger \mid \psi_i \rangle|^2$, hence

$$\frac{W_{if}^{abs}}{\rho(E_f)\big|_{E_f = E_i + \hbar\omega}} = \frac{W_{if}^{emi}}{\rho(E_f)\big|_{E_f = E_i - \hbar\omega}}. \tag{10.59}$$

This relation is known as the condition of *detailed balancing*.

Example 10.1

A particle, which is initially ($t = 0$) in the ground state of an infinite, one-dimensional potential box with walls at $x = 0$ and $x = a$, is subjected for $0 \leq t \leq \infty$ to a perturbation $\hat{V}(t) = \hat{x}^2 e^{-t/\tau}$. Calculate to first order the probability of finding the particle in its first excited state for $t \geq 0$.

Solution

For a particle in a box potential, with $E_n = n^2\pi^2\hbar^2/(2ma^2)$ and $\psi_n(x) = \sqrt{2/a}\sin(n\pi x/a)$, the ground state corresponds to $n = 1$ and the first excited state to $n = 2$. We can use (10.41) to obtain

$$P_{12} = \frac{1}{\hbar^2} \left| \int_0^\infty \langle \psi_2 | \hat{V}(t) | \psi_1 \rangle e^{i\omega_{21} t} dt \right|^2 = \frac{1}{\hbar^2} \left| \langle \psi_2 | \hat{x}^2 | \psi_1 \rangle \right|^2 \left| \int_0^\infty e^{-(1/\tau - i\omega_{21})t} dt \right|^2, \tag{10.60}$$

where

$$\langle \psi_2 | \hat{x}^2 | \psi_1 \rangle = \int_0^a x^2 \psi_2^*(x) \psi_1(x)\, dx = \frac{2}{a} \int_0^a x^2 \sin\left(\frac{2\pi x}{a}\right) \sin\left(\frac{\pi x}{a}\right) dx = -\frac{16a^2}{9\pi^2}, \tag{10.61}$$

$$\left| \int_0^t e^{-(1/\tau - i\omega_{21})t} dt \right|^2 = \left| \frac{e^{-(1/\tau - i\omega_{21})t} - 1}{1/\tau - i\omega_{21}} \right|^2 = \frac{1 + e^{-2t/\tau} - 2e^{-t/\tau}\cos(\omega_{21}t)}{\omega_{21}^2 + 1/\tau^2}, \quad (10.62)$$

which, in the limit $t \to \infty$, reduces to

$$\left| \int_0^\infty e^{-(1/\tau - i\omega_{21})t} dt \right|^2 = \left[\omega_{21}^2 + \frac{1}{\tau^2} \right]^{-1} = \left[\frac{9\pi^4\hbar^2}{4m^2a^4} + \frac{1}{\tau^2} \right]^{-1}, \quad (10.63)$$

since $\omega_{21} = (E_2 - E_1)/\hbar = 3\pi^2\hbar/(2ma^2)$. A substitution of (10.61) and (10.63) into (10.60) leads to

$$P_{12} = \left(\frac{16a^2}{9\pi^2\hbar} \right)^2 \left[\frac{9\pi^4\hbar^2}{4m^2a^4} + \frac{1}{\tau^2} \right]^{-1}. \quad (10.64)$$