Photodissociation

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1 Bound-bound transitions

Consider a system that is described by a Hamiltonian with a time independent part $\hat{H}_0$ and a time dependent perturbation $V(t)$:

$$\hat{H} = \hat{H}_0 + V(t). \tag{1}$$

Furthermore, assume that the eigenvalues and eigenfunctions of $\hat{H}_0$ are known:

$$\hat{H}_0 |\, n\rangle = \epsilon_n |\, n\rangle, \tag{2}$$

and that the $|\, n\rangle$ are bound states, so that we can write

$$\langle\, n |\, m\rangle = \delta_{nm}. \tag{3}$$

The objective is to solve the time dependent Schrödinger equation

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t}\psi(t) = \hat{H}\psi(t), \tag{4}$$

subject to the condition that the initial state of the system is given by one of the bound states:

$$\psi(0) = |\, i\rangle. \tag{5}$$

We can now expand $\psi(t)$ in terms of the bound states of $\hat{H}_0$, using time dependent expansion coefficients

$$\psi(t) = \sum_n c_n(t) |\, n\rangle, \tag{6}$$

where we know from condition (5) that

$$c_n(0) = \delta_{ni}. \tag{7}$$

Inserting expansion (6) and Hamiltonian (1) into the Schrödinger equation (4) gives us

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \sum_n c_n(t) |\, n\rangle = \sum_m \epsilon_m c_m(t) |\, m\rangle + V(t) c_m(t) |\, m\rangle. \tag{8}$$

If we project from the left with a final state $\langle\, f\,|$, we get (using the orthonormality of the bound states)

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} c_f(t) = \epsilon_f c_f(t) + \sum_m \mathbb{V}_{fm}(t) c_m(t), \tag{9}$$

where we have defined the $\mathbb{V}$ matrix with elements

$$\mathbb{V}_{nm}(t) \equiv \langle\, n \,|\, V(t) \,|\, m \rangle. \tag{10}$$

If we now write the expansion coefficients $c_f(t)$ as [1]

$$c_f(t) = b_f(t) e^{-\frac{i}{\hbar}\epsilon_f t}, \tag{11}$$

the left hand side of equation (9) turns into

$$\begin{aligned} i\hbar \frac{\mathrm{d}c_f(t)}{\mathrm{d}t} &= i\hbar \frac{\mathrm{d}b_f(t)}{\mathrm{d}t} e^{-\frac{i}{\hbar}\epsilon_f t} + i\hbar b_f(t) \left[\frac{\mathrm{d}}{\mathrm{d}t} e^{-\frac{i}{\hbar}\epsilon_f t} \right] \\ &= i\hbar \frac{\mathrm{d}b_f(t)}{\mathrm{d}t} e^{-\frac{i}{\hbar}\epsilon_f t} + \epsilon_f b_f(t) e^{-\frac{i}{\hbar}\epsilon_f t} \\ &= i\hbar \frac{\mathrm{d}b_f(t)}{\mathrm{d}t} e^{-\frac{i}{\hbar}\epsilon_f t} + \epsilon_f c_f(t). \end{aligned} \tag{12}$$

Inserting this result in equation (9) leads to

$$i\hbar \frac{\mathrm{d}b_f(t)}{\mathrm{d}t} e^{-\frac{i}{\hbar}\epsilon_f t} = \sum_m \mathbb{V}_{fm}(t) b_m(t) e^{-\frac{i}{\hbar}\epsilon_m t}, \tag{13}$$

so that

$$i\hbar \frac{\mathrm{d}b_f(t)}{\mathrm{d}t} = \sum_m \mathbb{V}_{fm}(t) b_m(t) e^{i\omega_{fm} t}, \tag{14}$$

with $\omega_{fm} = (\epsilon_f - \epsilon_m)/\hbar$.

We now try to solve this equation, using some perturbation theory. If we write $\mathbb{V}$ as $\lambda\mathbb{W}$ for some $\lambda \in [0,1]$, expand the $b_f(t)$ in terms of this perturbation parameter:

$$b_f(t) = b_f^{(0)}(t) + \lambda b_f^{(1)}(t) + \ldots \tag{15}$$

[1] In the case that $V(t) = 0$, the solution to equation (9) is easily found to be $c_f(t) = c_f(0) \exp[-\frac{i}{\hbar}\epsilon_f t]$.

and neglect higher order terms, equation (14) reads

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left[b_f^{(0)}(t)+\lambda b_f^{(1)}(t)\right]=\sum_m \lambda \mathbb{W}_{fm}\left[b_m^{(0)}(t)+\lambda b_m^{(1)}(t)\right]e^{i\omega_{fm}t}. \tag{16}$$

Collecting equal powers of λ on both sides of the equation gives us

$$\begin{aligned}
\lambda^0: \qquad i\hbar\frac{\mathrm{d}}{\mathrm{d}t}b_f^{(0)}(t) &= 0, && (17)\\
\lambda^1: \qquad i\hbar\frac{\mathrm{d}}{\mathrm{d}t}b_f^{(1)}(t) &= \sum_m \mathbb{W}_{fm}(t)b_m^{(0)}(t)e^{i\omega_{fm}t}. && (18)
\end{aligned}$$

Since we know from equation (7) that $c_m(0)=\delta_{mi}$, and because the $b_m^{(0)}$ do not change with time, we find that $b_m^{(0)}(t)=b_m^{(0)}(0)=\delta_{mi}$, and hence

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}b_f^{(1)}(t)=\mathbb{W}_{fi}(t)e^{i\omega_{fi}t}. \tag{19}$$

At $t=0$, the system is unperturbed, so that $b_f(0)=b_f^{(0)}(0)$, and $b_f^{(1)}(0)=0$. Hence we can write the solution to equation (19) as

$$i\hbar b_f^{(1)}(t)=\int_0^t \mathbb{W}_{fi}(t')e^{i\omega_{fi}t'}\mathrm{d}t', \tag{20}$$

so that for $\lambda=1$

$$b_f^{(1)}(t)=-\frac{i}{\hbar}\int_0^t \mathbb{V}_{fi}(t')e^{i\omega_{fi}t'}\mathrm{d}t'. \tag{21}$$

Now consider the case where the time dependent perturbation $V(t)$ is caused by a photon:

$$V(t)=\mathbf{E}(t)\cdot\boldsymbol{\mu}=\mathbf{E}_0\cdot\boldsymbol{\mu}\cos\omega t \qquad (\omega>0), \tag{22}$$

where $\mathbf{E}_0$ is the electric field vector associated with the photon, and $\boldsymbol{\mu}$ is the transition dipole vector operator. Defining $\mathbb{V}_{fi}=\langle\, f\,|\,\mathbf{E}_0\cdot\boldsymbol{\mu}\,|\,i\rangle$ and rewriting $\cos\omega t$ as $\frac{1}{2}(\exp[i\omega t]+\exp[-i\omega t])$, we see that the coefficients $b_f^{(1)}(t)$ are given by

$$\begin{aligned}
b_f^{(1)}(t) &= -\frac{i}{\hbar}\int_0^t \mathbb{V}_{fi}\frac{1}{2}\left(e^{i\omega t'}+e^{-i\omega t'}\right)e^{i\omega_{fi}t'}\mathrm{d}t'\\
&= -\frac{i}{2\hbar}\mathbb{V}_{fi}\int_0^t\left(e^{i(\omega_{fi}+\omega)t'}+e^{i(\omega_{fi}-\omega)t'}\right)\mathrm{d}t'\\
&= -\frac{1}{2\hbar}\mathbb{V}_{fi}\left(\frac{e^{i(\omega_{fi}+\omega)t}-1}{\omega_{fi}+\omega}+\frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega}\right).
\end{aligned} \tag{23}$$

Since we are looking at an absorption process, $\omega_{fi}=(\epsilon_f-\epsilon_i)/\hbar>0$, so that the second (resonant) term of equation (23) becomes much larger than the first (anti-resonant) term if $\omega \approx \omega_{fi}$. So we can introduce another approximation ("rotating wave approximation"), that neglects the anti-resonant term. Introducing $\Delta\omega \equiv \omega_{fi} - \omega$, we can write

$$\begin{aligned} b_f^{(1)}(t) &= -\frac{1}{2\hbar}\mathbb{V}_{fi}\frac{e^{i\Delta\omega t}-1}{\Delta\omega} \\ &= -\frac{i}{\hbar}\mathbb{V}_{fi}\frac{e^{i\Delta\omega t/2}-e^{-i\Delta\omega t/2}}{2i\Delta\omega}e^{i\Delta\omega t/2} \\ &= -\frac{i}{\hbar}\mathbb{V}_{fi}\frac{\sin(\Delta\omega t/2)}{\Delta\omega}e^{i\Delta\omega t/2} \\ &= -\frac{i}{\hbar}\mathbb{V}_{fi}\,\mathrm{sinc}\,(\Delta\omega t/2)\frac{t}{2}e^{i\Delta\omega t/2}, \end{aligned} \tag{24}$$

where we have introduced the sinc function: $\mathrm{sinc}\, x = \sin x/x$. The final wave function then reads

$$\begin{aligned} \psi(t) &= \sum_f c_f(t)|\,f\rangle \\ &= \sum_f b_f(t)e^{-\frac{i}{\hbar}\epsilon_f t}|\,f\rangle \\ &= \sum_f [b_f^{(0)}(t)+b_f^{(1)}(t)]e^{-\frac{i}{\hbar}\epsilon_f t}|\,f\rangle \\ &= \sum_f [\delta_{fi}e^{-i\omega_f t}+b_f^{(1)}(t)]e^{-\frac{i}{\hbar}\epsilon_f t}|\,f\rangle \\ &= e^{-i\omega_i t}|\,i\rangle + \sum_f b_f^{(1)}(t)e^{-\frac{i}{\hbar}\epsilon_f t}|\,f\rangle \end{aligned} \tag{25}$$

Hence, the probability of being in a final state $f \neq i$ after a time t is given by

$$\begin{aligned} P_f(t) &= |\langle\, f|\,\psi(t)\rangle|^2 \\ &= |b_f^{(1)}(t)|^2 \\ &= \frac{t^2}{4\hbar^2}|\mathbb{V}_{fi}|^2\,\mathrm{sinc}^2(\Delta\omega t/2). \end{aligned} \tag{26}$$

A representation of the δ-function is given by

$$\begin{aligned} \delta(x) &= \lim_{\epsilon\to 0}\frac{\epsilon}{\pi}\frac{\sin^2(x/\epsilon)}{x^2} \\ &= \lim_{t\to\infty}\frac{1}{\pi t}\frac{\sin^2(xt)}{x^2} \\ &= \lim_{t\to\infty}\frac{t}{\pi}\,\mathrm{sinc}^2(xt), \end{aligned} \tag{27}$$

so that for sufficiently large t we can write

$$P_f(t) = \frac{\pi}{4\hbar^2}|\mathbb{V}_{fi}|^2\delta(\Delta\omega/2)t, \tag{28}$$

and, since $\delta(\alpha x) = |\alpha|^{-1}\delta(x)$

$$P_f(t) = \frac{\pi}{2\hbar^2}|\mathbb{V}_{fi}|^2\delta(\Delta\omega)t, \tag{29}$$

In equation (29), t must be large enough to justify the use of the δ-function. On the other hand, a large t means a large transition probability, which in turn means a large $|b_f^{(1)}(t)|$, so that the first-order perturbation approach breaks down. Hence, equation (29) is only valid for a limited range of time.

The question is now how to derive a formula for the cross section from the transition probability equation (29). To that end we look at a one-dimensional case, and define an energy density at point x and time t: $W(x,t)$. The total amount of energy at time t up to point x is denoted by $N(x,t)$:

$$N(x,t) = \int_{-\infty}^{x} \mathrm{d}x' W(x',t). \tag{30}$$

Assuming that the energy is coming from a source (or going into a sink) $S(x,t)$, and denoting the intensity at point x, or energy flux through x, by $I(x,t)$, we can construct an energy balance

$$\frac{\partial}{\partial t}N(x,t) = -I(x,t) + \int_{-\infty}^{x} \mathrm{d}x' S(x',t). \tag{31}$$

Hence, the energy density changes in time as

$$\frac{\partial}{\partial t}W(x,t) = \frac{\partial}{\partial t}\frac{\partial}{\partial x}N(x,t) = \frac{\partial}{\partial x}\frac{\partial}{\partial t}N(x,t) = S(x,t) - \frac{\partial}{\partial x}I(x,t). \tag{32}$$

Now consider the case where absorption is weak, so that $S(x,t)$ is approximately zero. We compute the speed at which we have to change x in time in such a way that the total amount of energy up to x stays the same:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}N(x(t),t) &= \frac{\mathrm{d}x(t)}{\mathrm{d}t}\frac{\partial}{\partial x}N(x(t),t) + \frac{\partial}{\partial t}N(x(t),t) \\ &= v(t)W(x(t),t) - I(x(t),t) = 0. \end{aligned} \tag{33}$$

However, this speed is exactly the speed of the moving photon, and hence $v(t)$ is constant and equal to the speed of light c, so that we get

$$W(x,t) = \frac{I(x,t)}{c}. \tag{34}$$

On the other hand, when absorption is weak, then the energy density is approximately constant in time. Then

$$\frac{\partial}{\partial t}W(x,t) = 0 \qquad \Rightarrow \qquad S(x,t) = \frac{\partial}{\partial x}I(x,t). \tag{35}$$

From Beer's law, we know that $I(x) = I_0 \exp[-\sigma(\omega)\rho x]$, with ρ being the molecule density and $\sigma(\omega)$ the frequency dependent cross section, so that

$$S(x) = -\sigma(\omega)\rho I(x). \tag{36}$$

Back in the real world, we can write the transition rate from $|\, i\rangle$ to $|\, f\rangle$ as

$$k_{fi} = \frac{\partial}{\partial t}P_f(t) = \frac{\pi}{2\hbar^2}|\mathbb{V}_{fi}|^2\delta(\Delta\omega). \tag{37}$$

Write the electric field vector as $\mathbf{E}_0 = E_0\mathbf{e}$, with $|\mathbf{e}| = 1$, and define the matrix elements $\mathbb{M}_{fi} \equiv \langle\, f \,|\, \mathbf{e}\cdot\boldsymbol{\mu} \,|\, i\rangle$, then equation (37) turns into

$$k_{fi} = \frac{\pi E_0^2}{2\hbar^2}|\mathbb{M}_{fi}|^2\delta(\Delta\omega). \tag{38}$$

The average energy density of the photon is given by $W = \epsilon_0 E_0^2/2$, and since we know from equation (34) that $W = I/c$, we can rewrite this as

$$k_{fi} = \frac{\pi I}{\hbar^2 c\epsilon_0}|\mathbb{M}_{fi}|^2\delta(\Delta\omega). \tag{39}$$

The total absorption is proportional to the product of the transition rate times the amount of energy per transition, and the density of molecules:

$$S(x) = -k_{fi}\hbar\omega_{fi}\rho. \tag{40}$$

Using equation (36) and filling in the expression for the rate constant we get

$$-\sigma(\omega)\rho I = -\frac{\pi I\omega_{fi}\rho}{\hbar c\epsilon_0}|\mathbb{M}_{fi}|^2\delta(\Delta\omega) \tag{41}$$

so that the cross section is given by

$$\sigma(\omega) = \frac{\pi\omega_{fi}}{\hbar c\epsilon_0}|\mathbb{M}_{fi}|^2\delta(\omega_{fi}-\omega). \tag{42}$$

2 Bound-continuum transitions

The derivation of the expressions from the previous section all rely on the fact that the states $|\, n\rangle$ of the system can be normalized, see equation (3). Clearly for continuum states, this is no longer possible, since these states behave like free waves for $R \to \infty$ instead of decaying to zero. Hence we must proceed in a different fashion to extend the theory to bound-continuum transitions. To that end, we define the function

$$\varphi_x(x') = \delta(x - x'), \tag{43}$$

and the projection

$$\langle\, x|\, \psi\rangle = (\varphi_x, \psi) \tag{44}$$

with

$$(\phi, \psi) = \int \phi^*(x)\psi(x)\mathrm{d}x. \tag{45}$$

Working out equation (44) gives

$$\langle\, x|\, \psi\rangle = \int \varphi_x^*(x')\psi(x')\mathrm{d}x' = \int \delta(x - x')\psi(x')\mathrm{d}x' = \psi(x), \tag{46}$$

and for the special case $\psi = \varphi_{x'}$, this reads

$$\langle\, x|\, x'\rangle = \varphi_{x'}(x) = \delta(x' - x). \tag{47}$$

All functions ψ can be expanded in terms of $|\, x\rangle \equiv \varphi_x$:

$$\begin{aligned}\langle\, x|\, \psi\rangle = \psi(x) = \int \delta(x - x')\psi(x)'\mathrm{d}x' = \int \psi(x')\varphi_x(x')\mathrm{d}x' = \int \psi(x')\langle\, x|\, x'\rangle\mathrm{d}x' \\ = \langle\, x| \int \psi(x')|\, x'\rangle\mathrm{d}x'\rangle.\end{aligned} \tag{48}$$

From this expression we see that

$$|\, \psi\rangle = \int \psi(x)|\, x\rangle\mathrm{d}x, \tag{49}$$

and thus

$$\langle\, \psi\,| = \int \psi^*(x)\langle\, x\,|\mathrm{d}x. \tag{50}$$

Using these expression for expansion of a function, we see that for arbitrary ϕ and ψ we have

$$\begin{aligned}\langle\, \phi\,| \left[\int |\, x\rangle\langle\, x\,|\mathrm{d}x\right] |\, \psi\rangle &= \int \mathrm{d}x' \int \mathrm{d}x''\phi^*(x')\psi(x'') \int \mathrm{d}x\langle\, x'|\, x\rangle\langle\, x|\, x''\rangle \\ &= \int \mathrm{d}x' \int \mathrm{d}x''\phi^*(x')\psi(x'') \int \mathrm{d}x\delta(x - x')\delta(x'' - x) \\ &= \int \mathrm{d}x' \int \mathrm{d}x''\phi^*(x')\psi(x'')\delta(x'' - x') \\ &= \int \mathrm{d}x'\phi^*(x')\psi(x') \\ &= \langle\, \phi|\, \psi\rangle,\end{aligned} \tag{51}$$

so that the operator $\int |\, x\rangle\langle\, x\,| \mathrm{d}x = \hat{1}$. Define the plane waves $|\, k\rangle$ by

$$\langle\, x |\, k\rangle = \frac{1}{\sqrt{2\pi}} e^{ikx}. \tag{52}$$

Using the closure of the $|\, x\rangle$, we can write

$$\begin{aligned}\langle\, k |\, k'\rangle &= \int \mathrm{d}x \langle\, k' |\, x\rangle\langle\, x |\, k\rangle = \int \mathrm{d}x \langle\, x |\, k'\rangle^* \langle\, x |\, k\rangle = \frac{1}{2\pi}\int \mathrm{d}x e^{i(k-k')x} \\ &= \delta(k'-k).\end{aligned} \tag{53}$$

The $|\, k\rangle$ also close to identity, since applying $\int \mathrm{d}k |\, k\rangle\langle\, k\,|$ to an arbitrary function ψ gives

$$\begin{aligned}\left[\int \mathrm{d}k |\, k\rangle\langle\, k\,|\right] |\, \psi\rangle &= \int \mathrm{d}k \int \mathrm{d}x |\, x\rangle\langle\, x |\, k\rangle \int \mathrm{d}x' \langle\, k |\, x'\rangle\langle\, x' |\, \psi\rangle \\ &= \frac{1}{2\pi}\int \mathrm{d}k \int \mathrm{d}x |\, x\rangle e^{ikx} \int \mathrm{d}x' e^{-ikx'}\psi(x') \\ &= \frac{1}{2\pi}\int \mathrm{d}k \int \mathrm{d}x |\, x\rangle \int \mathrm{d}x' e^{ik(x-x')}\psi(x') \\ &= \int \mathrm{d}x |\, x\rangle \int \mathrm{d}x' \delta(x'-x)\psi(x') \\ &= \int \mathrm{d}x \psi(x) |\, x\rangle \\ &= |\, \psi\rangle.\end{aligned} \tag{54}$$

The plane waves are eigenfunctions of the momentum operator $\hat{p}$:[2]

$$\begin{aligned}\langle\, x\,|\, \hat{p}\,|\, k\rangle &= \int \mathrm{d}x' \langle\, x\,|\, \hat{p}\,|\, x'\rangle\langle\, x' |\, k\rangle \\ &= \frac{-i\hbar}{\sqrt{2\pi}}\int \mathrm{d}x' \frac{\partial}{\partial x}\delta(x'-x)e^{ikx'} \\ &= \frac{-i\hbar}{\sqrt{2\pi}}\frac{\partial}{\partial x}e^{ikx} \\ &= \hbar k \frac{1}{\sqrt{2\pi}}e^{ikx} \\ &= \hbar k \langle\, x |\, k\rangle,\end{aligned} \tag{55}$$

so that $\hat{p} |\, k\rangle = \hbar k |\, k\rangle$. Of course, the effect of the kinetic energy operator $\hat{T} = \hat{p}^2/2\mu$ on a plane wave is then given by

$$\hat{T} |\, k\rangle = \frac{\hbar^2 k^2}{2\mu} |\, k\rangle \equiv \hbar\omega_k |\, k\rangle. \tag{56}$$

[2]Postulate: $[\hat{x},\hat{p}] = i\hbar$. Then $\langle\, x\,|\, [\hat{x},\hat{p}]\,|\, x'\rangle = i\hbar\langle\, x |\, x'\rangle = i\hbar\delta(x'-x)$. But also $\langle\, x\,|\, [\hat{x},\hat{p}]\,|\, x'\rangle = \langle\, x\,|\, \hat{x}\hat{p} - \hat{p}\hat{x}\,|\, x'\rangle = (x-x')\langle\, x\,|\, \hat{p}\,|\, x'\rangle$, so that $(x-x')\langle\, x\,|\, \hat{p}\,|\, x'\rangle = i\hbar\delta(x-x')$, with solution $\langle\, x\,|\, \hat{p}\,|\, x'\rangle = -i\hbar\frac{\partial}{\partial x}\delta(x'-x)$.

We can extend this to three dimensions, defining

$$|\,\mathbf{k}\rangle = |\,k_x\rangle|\,k_y\rangle|\,k_z\rangle \qquad \text{and} \qquad |\,\mathbf{r}\rangle = |\,x\rangle|\,y\rangle|\,z\rangle, \tag{57}$$

so that, analogous to the one-dimensional case, we can write

$$\langle\,\mathbf{r}|\,\mathbf{k}\rangle = \frac{1}{\sqrt{2\pi}}e^{ik_x x}\frac{1}{\sqrt{2\pi}}e^{ik_y y}\frac{1}{\sqrt{2\pi}}e^{ik_z z} = \frac{1}{(2\pi)^{\frac{3}{2}}}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{58}$$

and since

$$\int \mathrm{d}\mathbf{r}|\,\mathbf{r}\rangle\langle\,\mathbf{r}\,| = \int \mathrm{d}x|\,x\rangle\langle\,x\,|\int \mathrm{d}y|\,y\rangle\langle\,y\,|\int \mathrm{d}z|\,z\rangle\langle\,z\,| = \hat{1}\hat{1}\hat{1} = \hat{1}, \tag{59}$$

we can also derive that

$$\langle\,\mathbf{k}|\,\mathbf{k}'\rangle = \delta(\mathbf{k}'-\mathbf{k}) \qquad \text{and} \qquad \int \mathrm{d}\mathbf{k}|\,\mathbf{k}\rangle\langle\,\mathbf{k}\,| = \hat{1}. \tag{60}$$

The effect of the kinetic energy operator can easily be derived, since

$$\begin{aligned}\hat{T}|\,\mathbf{k}\rangle &= \frac{1}{2\mu}(\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2)|\,\mathbf{k}\rangle \\ &= \frac{\hbar^2}{2\mu}(k_x^2+k_y^2+k_z^2)|\,\mathbf{k}\rangle \\ &= \frac{\hbar^2 k^2}{2\mu}|\,\mathbf{k}\rangle, \qquad (=\hbar\omega_k|\,\mathbf{k}\rangle)\end{aligned} \tag{61}$$

where k is the length of $\mathbf{k}$.

Consider a two-part system with a time-independent Hamiltonian $\hat{H} = \hat{T} + V$, where V is the interaction potential. We can write down the Schrödinger equations

$$i\hbar\frac{\partial}{\partial t}\psi(t) = \hat{H}\psi(t), \tag{62}$$

$$i\hbar\frac{\partial}{\partial t}\psi_0(t) = \hat{T}\psi_0(t), \tag{63}$$

and their formal solutions

$$\psi(t) = e^{-i\hat{H}(t-t_0)/\hbar}\psi(t_0), \tag{64}$$

$$\psi_0(t) = e^{-i\hat{T}(t-t_0)/\hbar}\psi_0(t_0). \tag{65}$$

If this system is a scattering system, then the two parts are infinitely separated when $t \to -\infty$, and the interaction potential is then zero. Hence, the two wave functions must be the same, so that

$$\lim_{t\to-\infty}||\psi(t)-\psi_0(t)|| = 0. \tag{66}$$

Substituting the formal solutions from equations (64) and (65) gives

$$\begin{aligned}&\lim_{t\to-\infty}||e^{-i\hat{H}(t-t_0)/\hbar}\psi(t_0)-e^{-i\hat{T}(t-t_0)/\hbar}\psi_0(t_0)||=\\&\lim_{t\to-\infty}||e^{-i\hat{H}(t-t_0)/\hbar}[\psi(t_0)-e^{i\hat{H}(t-t_0)/\hbar}e^{-i\hat{T}(t-t_0)/\hbar}\psi_0(t_0)]||=\\&\lim_{t\to-\infty}||\psi(t_0)-e^{i\hat{H}(t-t_0)/\hbar}e^{-i\hat{T}(t-t_0)/\hbar}\psi_0(t_0)||=0,\end{aligned}\tag{67}$$

and thus

$$\psi(t_0)=\lim_{t\to-\infty}e^{i\hat{H}t/\hbar}e^{-i\hat{T}t/\hbar}\psi_0(t_0).\tag{68}$$

The operator $\lim_{t\to-\infty}\exp[i\hat{H}t/\hbar]\exp[-i\hat{T}t/\hbar]$ is called the Møller wave operator, and is denoted by Ω^+. This operator holds the boundary conditions for the wave functions since it specifies what the system must look like: going back in time with the unperturbed Hamiltonian (until the system consists of free particles) and then forward again with the perturbation turned on. Since equation (68) holds for any t_0, we can write

$$\psi(t)=\Omega^+\psi_0(t).\tag{69}$$

Writing out the exponent of $\hat{T}$ working on a plane wave $|\,\mathbf{k}\rangle$ gives

$$e^{\hat{T}}|\,\mathbf{k}\rangle=\sum_{j=0}^{\infty}\frac{1}{j!}\hat{T}^j|\,\mathbf{k}\rangle=\sum_{j=0}^{\infty}\frac{1}{j!}(\hbar\omega_k)^j|\,\mathbf{k}\rangle=e^{\hbar\omega_k}|\,\mathbf{k}\rangle,\tag{70}$$

so that operating with the Møller operator on a plane wave gives

$$\Omega^+|\,\mathbf{k}\rangle=\lim_{t\to-\infty}e^{i\hat{H}t/\hbar}e^{-i\hat{T}t/\hbar}|\,\mathbf{k}\rangle=\lim_{t\to-\infty}e^{i(\hat{H}-\hbar\omega_k)t/\hbar}|\,\mathbf{k}\rangle.\tag{71}$$

Using the relation [3]

$$\lim_{t\to-\infty}f(t)=\lim_{\epsilon\to0^+}\int_{-\infty}^{0}\epsilon e^{\epsilon t}f(t)\mathrm{d}t,\tag{72}$$

[3] Suppose that $\lim_{t\to-\infty}f(t)$ exists. Then, split the integral into two parts:

$$\lim_{\epsilon\to0^+}\left[\int_{-\infty}^{T}\epsilon\exp[\epsilon t]f(t)\mathrm{d}t+\int_{T}^{0}\epsilon\exp[\epsilon t]f(t)\mathrm{d}t\right]$$

For every finite T, the second term is zero if $f(t)$ is finite, since ϵ goes to zero. Since $\lim_{t\to-\infty}f(t)$ exists, we can get arbitrarily close to the limiting value of f, by choosing a small enough T, so that f is approximately constant over the integration range. Denoting this limit by $f(-\infty)$, we then get

$$\lim_{\epsilon\to0^+}f(-\infty)\int_{-\infty}^{T}\epsilon\exp[\epsilon t]\mathrm{d}t=f(-\infty)\lim_{\epsilon\to0^+}\exp[\epsilon t]\Big|_{-\infty}^{T}=f(-\infty).$$

we then see that

$$
\begin{aligned}
\Omega^{+}|\,\mathbf{k}\rangle &= \lim_{\epsilon\to 0^{+}} \int_{-\infty}^{0} \epsilon e^{i(\hat{H}-\hbar\omega_k - i\hbar\epsilon)t/\hbar} \mathrm{d}t|\,\mathbf{k}\rangle \\
&= \lim_{\epsilon\to 0^{+}} -i\hbar\epsilon(\hat{H}-\hbar\omega_k - i\hbar\epsilon)^{-1} e^{i(\hat{H}-\hbar\omega_k - i\hbar\epsilon)t/\hbar}\Big|_{-\infty}^{0} |\,\mathbf{k}\rangle \\
&= \lim_{\epsilon\to 0^{+}} i\hbar\epsilon(\hbar\omega_k + i\hbar\epsilon - \hat{H})^{-1}|\,\mathbf{k}\rangle .
\end{aligned} \tag{73}
$$

Denote the result by the ket $|\,\psi_{\mathbf{k}}^{+}\rangle$, i.e.

$$
\begin{aligned}
|\,\psi_{\mathbf{k}}^{+}\rangle &\equiv \lim_{\epsilon\to 0^{+}} i\hbar\epsilon(\hbar\omega_k + i\hbar\epsilon - \hat{H})^{-1}|\,\mathbf{k}\rangle \\
&= \lim_{\epsilon\to 0^{+}} i\hbar\epsilon\hat{G}(\hbar\omega_k + i\hbar\epsilon)|\,\mathbf{k}\rangle ,
\end{aligned} \tag{74}
$$

where $\hat{G}(\hbar\omega_k + i\hbar\epsilon)$ is the Green's function for $\hat{H}$.

2.1 Intermezzo: Green's functions

A simple example of the use of Green's function is used to solve the system

$$
\begin{cases} \frac{\mathrm{d}}{\mathrm{d}x} f(x) = h(x) \\ f(A) = 0 \end{cases} \tag{75}
$$

on the interval $\langle A, B\rangle$. The solution is of course given by

$$
f(x) = \int_A^x h(x')\mathrm{d}x' . \tag{76}
$$

Using Green's functions we would write the solution as

$$
f(x) = \int_A^B g(x,x')h(x')\mathrm{d}x' , \tag{77}
$$

with, in this case

$$
g(x,x') = \theta(x-x') = \begin{cases} 1 & x > x' \\ 0 & x < x' \end{cases} . \tag{78}
$$

Using the original differential equation, we know that

$$
\frac{\mathrm{d}}{\mathrm{d}x}\int_A^B g(x,x')h(x')\mathrm{d}x' = \int_A^B \frac{\mathrm{d}}{\mathrm{d}x} g(x,x')h(x')\mathrm{d}x' = h(x), \tag{79}
$$

from which follows that $\frac{\mathrm{d}}{\mathrm{d}x}g(x,x') = \delta(x-x')$, and thus that $\frac{\mathrm{d}}{\mathrm{d}x}g(x,x') = 0$ whenever $x \neq x'$. More generally, when trying to solve a differential equation

$$\hat{D}(x)f(x) = h(x), \tag{80}$$

where $\hat{D}(x)$ is a differential operator, we can find the Green's function for that system by solving

$$\hat{D}(x)g(x,x') = 0 \tag{81}$$

for $x \neq x'$, and connecting the solutions in such a way that

$$\hat{D}(x)g(x,x') = \delta(x-x') \qquad \Rightarrow \qquad \int \hat{D}(x)g(x,x')\mathrm{d}x' = 1. \tag{82}$$

The problem we are trying to solve is

$$\hat{H}|\,\psi\rangle = [\hat{T} + V]|\,\psi\rangle = E|\,\psi\rangle \tag{83}$$

so that

$$[E - \hat{T}]|\,\psi\rangle = V|\,\psi\rangle \qquad \Rightarrow \qquad |\,\psi\rangle = [E-\hat{T}]^{-1}V|\,\psi\rangle. \tag{84}$$

We denote the operator $[E-\hat{T}]^{-1}$ by $\hat{G}_0(E)$. An explicit expression for this operator can be obtained by inserting a resolution of identity:

$$|\,\psi\rangle = \int \mathrm{d}\mathbf{k}[E-\hat{T}]^{-1}|\,\mathbf{k}\rangle\langle\,\mathbf{k}\,|\,V\,|\,\psi\rangle = \int \mathrm{d}\mathbf{k}\frac{1}{E-\hbar\omega_k}|\,\mathbf{k}\rangle\langle\,\mathbf{k}\,|\,V\,|\,\psi\rangle, \tag{85}$$

so that

$$\hat{G}_0(E) = \int \mathrm{d}\mathbf{k}\frac{|\,\mathbf{k}\rangle\langle\,\mathbf{k}\,|}{E-\hbar\omega_k}. \tag{86}$$

Writing

$$\langle\,\mathbf{r}\,|\,\hat{G}_0(E)\,|\,\mathbf{r}'\rangle = \int \mathrm{d}\mathbf{k}\frac{\langle\,\mathbf{r}|\,\mathbf{k}\rangle\langle\,\mathbf{k}|\,\mathbf{r}'\rangle}{E-\hbar\omega_k} = g_0(\mathbf{r},\mathbf{r}') \tag{87}$$

we see that

$$\begin{aligned} \psi(\mathbf{r}) = \langle\,\mathbf{r}|\,\psi\rangle &= \int \mathrm{d}\mathbf{r}' \int \mathrm{d}\mathbf{r}''\langle\,\mathbf{r}\,|\,\hat{G}_0(E)\,|\,\mathbf{r}'\rangle\langle\,\mathbf{r}'\,|\,V\,|\,\mathbf{r}''\rangle\langle\,\mathbf{r}''|\,\psi\rangle \\ &= \int \mathrm{d}\mathbf{r}' \int \mathrm{d}\mathbf{r}'' g_0(\mathbf{r},\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r}'')V(\mathbf{r}')\psi(\mathbf{r}'') \\ &= \int \mathrm{d}\mathbf{r}' g_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}'). \end{aligned} \tag{88}$$

Alternatively, since $\hat{H}|\,\psi\rangle = E|\,\psi\rangle$, we could have written

$$|\,\psi\rangle = [E-\hat{H}]^{-1}|\,\psi\rangle \equiv \hat{G}(E)|\,\psi\rangle, \tag{89}$$

thus defining the Green's operator

$$\hat{G}(E) = [E-\hat{H}]^{-1}, \tag{90}$$

see also equation (74).

The two Green's operator $\hat{G}_0(E)$ and $\hat{G}(E)$ can be related. Since

$$\hat{G}(E)[E-\hat{H}] = \hat{1}, \tag{91}$$

and $\hat{H} = \hat{T} + V$, we know that

$$[E-\hat{T}-V]\hat{G}(E) = [E-\hat{T}]\hat{G}(E) - V\hat{G}(E) = \hat{1}. \tag{92}$$

Multiplying from the left with $\hat{G}_0(E)$ gives

$$\hat{G}(E) - \hat{G}_0(E)V\hat{G}(E) = \hat{G}_0(E) \tag{93}$$

so that

$$\hat{G}(E) = \hat{G}_0(E) + \hat{G}_0(E)V\hat{G}(E). \tag{94}$$

End of intermezzo □

Defining $\hat{G}^+(\hbar\omega_k) \equiv \hat{G}(\hbar\omega_k + i\hbar\epsilon)$, we use equation (94) to write $|\,\psi_{\mathbf{k}}^+\rangle$ as

$$\begin{aligned} |\,\psi_{\mathbf{k}}^+\rangle &= \lim_{\epsilon\to 0^+} i\hbar\epsilon\hat{G}_0^+(\hbar\omega_k)|\,\mathbf{k}\rangle + i\hbar\epsilon\hat{G}_0^+(\hbar\omega_k)V\hat{G}^+(\hbar\omega_k)|\,\mathbf{k}\rangle \\ &= \lim_{\epsilon\to 0^+} i\hbar\epsilon\hat{G}_0^+(\hbar\omega_k)|\,\mathbf{k}\rangle + \hat{G}_0^+(\hbar\omega_k)V|\,\psi_{\mathbf{k}}^+\rangle. \end{aligned} \tag{95}$$

Working out the effect of $\hat{G}_0^+(\hbar\omega_k)$ on $|\,\mathbf{k}\rangle$ shows that

$$\begin{aligned} \lim_{\epsilon\to 0^+} i\hbar\epsilon\hat{G}_0^+(\hbar\omega_k)|\,\mathbf{k}\rangle &= \lim_{\epsilon\to 0^+} \frac{i\hbar\epsilon}{\hbar\omega_k + i\hbar\epsilon - \hat{T}}|\,\mathbf{k}\rangle \\ &= \lim_{\epsilon\to 0^+} \frac{i\hbar\epsilon}{\hbar\omega_k + i\hbar\epsilon - \hbar\omega_k}|\,\mathbf{k}\rangle \\ &= |\,\mathbf{k}\rangle, \end{aligned} \tag{96}$$

so that

$$|\,\psi_{\mathbf{k}}^+\rangle = |\,\mathbf{k}\rangle + \hat{G}_0^+(\hbar\omega_k)V|\,\psi_{\mathbf{k}}^+\rangle. \tag{97}$$

This result now defines the boundary conditions for a scattering state, given by

$$\begin{aligned} \langle\,\mathbf{r}|\,\psi_{\mathbf{k}}^+\rangle &= \langle\,\mathbf{r}|\,\mathbf{k}\rangle + \int \mathrm{d}\mathbf{r}'\langle\,\mathbf{r}\,|\,\hat{G}_0^+(\hbar\omega_k)\,|\,\mathbf{r}'\rangle\langle\,\mathbf{r}'\,|\,V\,|\,\psi_{\mathbf{k}}^+\rangle \\ &= \frac{1}{(2\pi)^{\frac{3}{2}}}e^{i\mathbf{k}\cdot\mathbf{r}} + \int \mathrm{d}\mathbf{r}' g_0^+(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi_{\mathbf{k}}^+(\mathbf{r}') \end{aligned} \tag{98}$$

which is of course nice, but pretty useless if we do not have an expression for $g_0^+(\mathbf{r},\mathbf{r}')$. This can be derived, however (which we will not), and the result is given by

$$g_0^+(\mathbf{r},\mathbf{r}') = -\frac{\mu}{2\pi\hbar^2|\mathbf{r}-\mathbf{r}'|}e^{ik|\mathbf{r}-\mathbf{r}'|}. \tag{99}$$

If we expand $|\mathbf{r}-\mathbf{r}'|$ in a Taylor polynomial around $r' = |\mathbf{r}'| = 0$, then in the limit of $r = |\mathbf{r}| \gg r'$, we can write the distance between the two points as

$$|\mathbf{r}-\mathbf{r}'| = r - \frac{\mathbf{r}\cdot\mathbf{r}'}{r} + \mathcal{O}\left(\frac{r'}{r}\right). \tag{100}$$

Using this equation, we can rewrite the Green's function to

$$g_0^+(\mathbf{r},\mathbf{r}') = -\frac{\mu}{2\pi\hbar^2 r}e^{ikr}\frac{kr}{kr-\mathbf{k}'\cdot\mathbf{r}'}e^{-i\mathbf{k}'\cdot\mathbf{r}'} \tag{101}$$

where $\mathbf{k}' \equiv k\mathbf{r}/r$. For sufficiently large r the second fraction goes to one, so that the scattering state looks like

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = \frac{1}{(2\pi)^{\frac{3}{2}}}e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2 r}e^{ikr}\int \mathrm{d}\mathbf{r}' e^{-i\mathbf{k}'\cdot\mathbf{r}'}V(\mathbf{r}')\psi_{\mathbf{k}}^+(\mathbf{r}'), \tag{102}$$

where the integral on the right hand side no longer depends on the length of $\mathbf{r}$, but only on its direction $\hat{\mathbf{r}}$. We can try to solve this equation iteratively, by starting with an approximation for $\psi_{\mathbf{k}}^+$, calculating the integral and using the result as a new approximation. Note that this function requires that the potential falls faster then $1/r$ in the long range, since the integration volume element $r^2\mathrm{d}r\mathrm{d}\hat{\mathbf{r}}$ grows quadratically in r, and for the plane waves

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi\sum_{l=0}^{\infty} i^l j_l(kr)\sum_{m=-l}^{l} Y_{lm}^*(\hat{\mathbf{k}})Y_{lm}(\hat{\mathbf{r}}), \tag{103}$$

the radial term $j_0(kr) = \sin(kr)/(kr)$ only falls as $1/r$. The first order approximation, with the initial guess $|\,\psi_{\mathbf{k}}^+\rangle = |\,\mathbf{k}\rangle$ is called the Born approximation, and is simply related to the Fourier transform of the potential, since

$$\begin{aligned}\psi_{\mathbf{k}}^+(\mathbf{r}) &\approx \frac{1}{(2\pi)^{\frac{3}{2}}}\left[e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2 r}e^{ikr}\int \mathrm{d}\mathbf{r}' e^{-i\mathbf{k}'\cdot\mathbf{r}'}V(\mathbf{r}')e^{i\mathbf{k}\cdot\mathbf{r}'}\right] \\ &= \langle\,\mathbf{r}|\,\mathbf{k}\rangle - \frac{\mu\sqrt{2\pi}}{\hbar^2 r}e^{ikr}\int \mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}''\langle\,\mathbf{k}'|\,\mathbf{r}'\rangle\langle\,\mathbf{r}'\,|\,V\,|\,\mathbf{r}''\rangle\langle\,\mathbf{r}''|\,\mathbf{k}\rangle \\ &= \langle\,\mathbf{r}|\,\mathbf{k}\rangle - \frac{\mu\sqrt{2\pi}}{\hbar^2 r}e^{ikr}\langle\,\mathbf{k}'\,|\,V\,|\,\mathbf{k}\rangle\end{aligned} \tag{104}$$

In photodissociation we start with a system in a bound state, which we excite to a dissociating state through a time dependent coupling in the Hamiltonian. We can depict this by

$$\mathbb{H}(t) = \begin{pmatrix} \mathbb{H}_g & \mathbb{W}(t) \\ \mathbb{W}(t) & \mathbb{H}_e\,, \end{pmatrix} \tag{105}$$

where $\hat{H}_g$ is the ground state Hamiltonian, and $\hat{H}_e$ is the excited state Hamiltonian. Suppose the bound states are known and normalized:

$$\hat{H}_g|\,i\rangle = \hbar\omega_i|\,i\rangle, \qquad \langle\,i|\,j\rangle = \delta_{ij}, \tag{106}$$

and set the phase at $t = 0$ to zero, so that $|\, i(t)\rangle = \exp[-i\omega_i t]|\, i\rangle$. Furthermore, we can write the excited state Hamiltonian as $\hat{H}_e = \hat{H}_{e,0} + V_e$, where the eigenstates of $\hat{H}_{e,0}$ are given by the plane waves

$$\hat{H}_{e,0}|\,\mathbf{k}\rangle = \hbar\omega_k|\,\mathbf{k}\rangle, \qquad \langle\,\mathbf{k}|\,\mathbf{k}'\rangle = \delta(\mathbf{k}' - \mathbf{k}) \tag{107}$$

with time evolution $|\,\mathbf{k}(t)\rangle = \exp[-i\omega_k t]|\,\mathbf{k}\rangle$. The Schrödinger equation may be familiar by now:

$$i\hbar\frac{\partial}{\partial t}|\,\psi(t)\rangle = \hat{H}(t)|\,\psi(t)\rangle. \tag{108}$$

Note that since the Hamiltonian depends on time, we cannot write a formal solution like $\psi(t) = \exp[-i\hat{H}(t)t/\hbar]\psi(0)$. Since we start in a bound state, we know that at the beginning of all times, the system must have been in one of the eigenstates of $\hat{H}_g$:

$$\lim_{t\to-\infty}|\,\psi(t)\rangle = |\,i(t)\rangle. \tag{109}$$

We split the Hamiltonian into a time-independent part $\hat{H}_0$ and a time-dependent perturbation $V(t)$, with matrix representations

$$\mathbb{H}_0 = \begin{pmatrix} \mathbb{H}_g & \mathbb{O} \\ \mathbb{O} & \mathbb{H}_e \end{pmatrix}, \qquad \mathbb{V}(t) = \begin{pmatrix} \mathbb{O} & \mathbb{W}(t) \\ \mathbb{W}(t) & \mathbb{O} \end{pmatrix}. \tag{110}$$

In order to get rid of as many trivial phase factors as possible, we define the function

$$\widetilde{\psi}(t) = e^{i\hat{H}_0 t/\hbar}\psi(t), \tag{111}$$

so that

$$\lim_{t\to-\infty}|\,\widetilde{\psi}(t)\rangle = \lim_{t\to-\infty}e^{i\hat{H}_0 t/\hbar}|\,i(t)\rangle = |\,i\rangle. \tag{112}$$

Inserting the definition of $\widetilde{\psi}(t)$ into the Schrödinger equation yields

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\,\widetilde{\psi}(t)\rangle &= i\hbar\left[\frac{\partial}{\partial t}e^{i\hat{H}_0 t/\hbar}\right]|\,\psi(t)\rangle + i\hbar e^{i\hat{H}_0 t/\hbar}\frac{\partial}{\partial t}|\,\psi(t)\rangle \\ &= e^{i\hat{H}_0 t/\hbar}[-\hat{H}_0 + \hat{H}(t)]|\,\psi(t)\rangle \\ &= e^{i\hat{H}_0 t/\hbar}V(t)e^{-i\hat{H}_0 t/\hbar}|\,\widetilde{\psi}(t)\rangle \\ &\equiv \widetilde{V}(t)|\,\widetilde{\psi}(t)\rangle. \end{aligned} \tag{113}$$

Integrating both sides from $-\infty$ to t gives

$$i\hbar\int_{-\infty}^{t}\frac{\partial}{\partial t'}|\,\widetilde{\psi}(t')\rangle\mathrm{d}t' = i\hbar[|\,\widetilde{\psi}(t)\rangle - |\,\widetilde{\psi}(-\infty)\rangle] = \int_{-\infty}^{t}\widetilde{V}(t')|\,\widetilde{\psi}(t')\rangle\mathrm{d}t', \tag{114}$$

so that

$$|\,\widetilde{\psi}(t)\rangle = |\,\widetilde{\psi}(-\infty)\rangle - \frac{i}{\hbar}\int_{-\infty}^{t}\widetilde{V}(t')|\,\widetilde{\psi}(t')\rangle\mathrm{d}t' = |\,i\rangle - \frac{i}{\hbar}\int_{-\infty}^{t}\widetilde{V}(t')|\,\widetilde{\psi}(t')\rangle\mathrm{d}t'. \tag{115}$$

In first order perturbation theory, this is

$$|\,\widetilde{\psi}(t)\rangle = |\,i\rangle - \frac{i}{\hbar}\int_{-\infty}^{t} \widetilde{V}(t')|\,i\rangle \mathrm{d}t'. \tag{116}$$

Hence, the first order correction to $|\,\widetilde{\psi}(t)\rangle$ is given by

$$|\,\widetilde{\psi}^{(1)}(t)\rangle = -\frac{i}{\hbar}\int_{-\infty}^{t} \widetilde{V}(t')|\,i\rangle \mathrm{d}t', \tag{117}$$

so that the first order correction to the original wave function is

$$|\,\psi^{(1)}(t)\rangle = -\frac{i}{\hbar}e^{-i\hat{H}_0 t/\hbar}\int_{-\infty}^{t} \widetilde{V}(t')|\,i\rangle \mathrm{d}t'. \tag{118}$$

Since the system is dissociating, we know that at the end of all times the wave function consists of free particle wave functions. Hence, we expand the wave function for large t in these functions:

$$|\,\psi^{(1)}(t)\rangle \xrightarrow{t\to\infty} \int \mathrm{d}\mathbf{k} f_{\mathbf{k}}(t)|\,\mathbf{k}(t)\rangle. \tag{119}$$

The expansion coefficients $f_{\mathbf{k}}(t)$ are by definition given by

$$f_{\mathbf{k}}(t) = \langle\,\mathbf{k}(t)|\,\psi^{(1)}(t)\rangle = -\frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' \langle\,\mathbf{k}(t)|\,e^{-i\hat{H}_0 t/\hbar}\widetilde{V}(t')i\rangle \tag{120}$$

Moving the exponent of $\hat{H}_0$ to the bra, and inserting the definition of $\langle\,\mathbf{k}(t)\,|$, we get

$$f_{\mathbf{k}}(t) = -\frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' \langle\,e^{i\hat{H}_0 t/\hbar}e^{-i\hat{H}_{e,0}t/\hbar}\mathbf{k}|\,\widetilde{V}(t')i\rangle. \tag{121}$$

The operator

$$\lim_{t\to\infty} e^{i\hat{H}_0 t/\hbar}e^{-i\hat{H}_{e,0}t/\hbar} \tag{122}$$

bears a striking resemblance to the Møller operator Ω^+ introduced in equation (68). The difference lies in the fact that with Ω^+ we first go back in time with the unperturbed operator, and then forward again with the perturbation on, whereas in equation (122) we go forward in time without perturbation and then back again (note that the ground state part $\hat{H}_g$ of $\hat{H}_0$ does not contribute, since $\exp[i\hat{H}_0 t/\hbar]$ operates on a plane wave). This difference is caused by the fact that the scattering system starts as a system of free particles, whereas in photodissociation we are going towards such a system. It will not come as a surprise, then, that the operator of equation (122) will be denoted by Ω^-.

Playing around a bit with the expansion coefficient turns equation (121) into

$$\begin{aligned} f_{\mathbf{k}}(t) &= -\frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' \langle\, \Omega^{-}\mathbf{k}|\, \widetilde{V}(t')i\rangle \\ &= -\frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' \langle\, \Omega^{-}\mathbf{k}|\, e^{i\hat{H}_0 t'/\hbar} V(t') e^{-i\hat{H}_0 t'/\hbar} i\rangle \\ &= -\frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' \langle\, e^{-i\hat{H}_0 t'/\hbar}\Omega^{-}\mathbf{k}|\, V(t') e^{-i\hat{H}_0 t'/\hbar} i\rangle. \end{aligned} \tag{123}$$

A nice property of the Møller operators is that it does not matter where the zero point of time is, i.e.

$$\begin{aligned} \Omega^{-} &= \lim_{t\to\infty} e^{i\hat{H}_0 t/\hbar} e^{-i\hat{H}_{e,0} t/\hbar} \\ &= \lim_{t\to\infty} e^{i\hat{H}_0 (t+t_0)/\hbar} e^{-i\hat{H}_{e,0} (t+t_0)/\hbar} \\ &= \lim_{t\to\infty} e^{i\hat{H}_0 t_0/\hbar} e^{i\hat{H}_0 t/\hbar} e^{-i\hat{H}_{e,0} t/\hbar} e^{-i\hat{H}_{e,0} t_0/\hbar} \\ &= e^{i\hat{H}_0 t_0/\hbar}\Omega^{-} e^{-i\hat{H}_{e,0} t_0/\hbar} \end{aligned} \tag{124}$$

for arbitrary t_0. Hence for arbitrary t we have

$$e^{-i\hat{H}_0 t/\hbar}\Omega^{-} = \Omega^{-} e^{-i\hat{H}_{e,0} t/\hbar}. \tag{125}$$

Applying this property to equation (123) gives

$$\begin{aligned} f_{\mathbf{k}}(t) &= -\frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' \langle\, \Omega^{-} e^{-i\hat{H}_{e,0} t'/\hbar}\mathbf{k}|\, V(t') e^{-i\hat{H}_0 t'/\hbar} i\rangle \\ &= -\frac{i}{\hbar}\int_{-\infty}^{t} \mathrm{d}t' e^{i(\omega_k-\omega_i)t'} \langle\, \Omega^{-}\mathbf{k}\,|\, V(t')\,|\, i\rangle. \end{aligned} \tag{126}$$

For a photon we have, as before, $V(t) = \mathbf{E}_0 \cdot \boldsymbol{\mu} \cos\omega t$, so that (denoting $\omega_k - \omega_i$ by ω_{ki})

$$f_{\mathbf{k}}(t) = -\frac{i}{\hbar}\langle\, \Omega^{-}\mathbf{k}\,|\, \mathbf{E}_0\cdot\boldsymbol{\mu}\,|\, i\rangle \int_{-\infty}^{t} \mathrm{d}t' e^{i\omega_{ki}t'} \cos\omega t'. \tag{127}$$

Applying the rotating wave approximation again, only the resonant part of the cosine, $\exp[-i\omega t']/2$, contributes. Suppose we "slowly turn on" the photon, by damping it with $\exp[\epsilon t]$ for some small, postive ϵ, then with $\Delta\omega = \omega_{ki} - \omega$ we get

$$f_{\mathbf{k}}(t) = \lim_{\epsilon\to 0^+} -\frac{i}{2\hbar}\langle\, \Omega^{-}\mathbf{k}\,|\, \mathbf{E}_0\cdot\boldsymbol{\mu}\,|\, i\rangle \int_{-\infty}^{t} \mathrm{d}t' e^{i(\Delta\omega - i\epsilon)t'}. \tag{128}$$

Working out the integral shows that

$$\begin{aligned} \int_{-\infty}^{t} \mathrm{d}t' e^{i(\Delta\omega-i\epsilon)t'} &= \int_{-\infty}^{0} \mathrm{d}t' e^{i(\Delta\omega-i\epsilon)t'} + \int_{0}^{t} \mathrm{d}t' e^{i(\Delta\omega-i\epsilon)t'} \\ &= \int_{0}^{\infty} \mathrm{d}t' e^{-i(\Delta\omega-i\epsilon)t'} + \int_{0}^{t} \mathrm{d}t' e^{i(\Delta\omega-i\epsilon)t'}. \end{aligned} \tag{129}$$

Due to the damping, the first function goes to zero when $t' \to \infty$, so that we can replace the integral from zero to infinity by one from zero to t, if we choose a large enough t:

$$\begin{aligned}
\int_{-\infty}^{t} \mathrm{d}t' e^{i(\Delta\omega - i\epsilon)t'} &= \int_{0}^{t} \mathrm{d}t' e^{-i(\Delta\omega - i\epsilon)t'} + e^{i(\Delta\omega - i\epsilon)t'} \\
&= 2\int_{0}^{t} \mathrm{d}t' \cos[(\Delta\omega - i\epsilon)t'] \\
&= 2\frac{\sin[(\Delta\omega - i\epsilon)t]}{\Delta\omega - i\epsilon} = 2t\,\mathrm{sinc}[(\Delta\omega - i\epsilon)t],
\end{aligned} \tag{130}$$

so that the expansion coefficients for the first order correction to the wave function are given by

$$f_{\mathbf{k}}(t) = -\frac{it}{\hbar}\langle\, \Omega^{-}\mathbf{k}\,|\,\mathbf{E}_0 \cdot \boldsymbol{\mu}\,|\, i\rangle\,\mathrm{sinc}[\Delta\omega t]. \tag{131}$$

Defining the matrix elements $\mathbb{M}_{\mathbf{k}i} \equiv \langle\, \Omega^{-}\mathbf{k}\,|\,\mathbf{e}\cdot\boldsymbol{\mu}\,|\,i\rangle$ we can then write the total wave function $|\,\psi(t)\rangle$ as

$$\begin{aligned}
|\,\psi(t)\rangle &= e^{-i\hat{H}_0 t/\hbar}|\,i\rangle + \int \mathrm{d}\mathbf{k} f_{\mathbf{k}}(t)|\,\mathbf{k}(t)\rangle \\
&= |\,i(t)\rangle - \frac{iE_0 t}{\hbar}\,\mathrm{sinc}[\Delta\omega t]\int \mathrm{d}\mathbf{k}\mathbb{M}_{\mathbf{k}i}|\,\mathbf{k}(t)\rangle.
\end{aligned} \tag{132}$$

We can then write an expression for the probability of being in a state $|\,\mathbf{k}(t)\rangle$ after a certain time t, since

$$\begin{aligned}
P_{\mathbf{k}}(t) &= |\langle\,\mathbf{k}(t)|\,\psi(t)\rangle|^2 \\
&= \frac{E_0^2 t^2}{\hbar^2}\,\mathrm{sinc}^2[\Delta\omega t]\Big|\int \mathrm{d}\mathbf{k}'\mathbb{M}_{\mathbf{k}'i}\langle\,\mathbf{k}(t)|\,\mathbf{k}'(t)\rangle\Big|^2 \\
&= \frac{E_0^2 t^2}{\hbar^2}\,\mathrm{sinc}^2[\Delta\omega t]\Big|\int \mathrm{d}\mathbf{k}'\mathbb{M}_{\mathbf{k}'i}\delta(\mathbf{k}'-\mathbf{k})\Big|^2 \\
&= \frac{E_0^2 t^2}{\hbar^2}\,\mathrm{sinc}^2[\Delta\omega t]|\mathbb{M}_{\mathbf{k}i}|^2.
\end{aligned} \tag{133}$$

Using equation (27), we rewrite this as

$$P_{\mathbf{k}}(t) = \frac{\pi E_0^2}{\hbar^2}|\mathbb{M}_{\mathbf{k}i}|^2\delta(\Delta\omega)t. \tag{134}$$

As noted before for the bound-bound transitions, this expression is only valid when t is large enough to justify the use of $\delta(\Delta\omega)$, but small enough to ensure that the first-order perturbation treatment is correct.

The transition rate from the initial state $|\,i\rangle$ to a scattering state $|\,\Omega^{-}\mathbf{k}\rangle$ is then simply given by

$$k_{\mathbf{k}i} = \frac{\pi E_0^2}{\hbar^2}|\mathbb{M}_{\mathbf{k}i}|^2\delta(\Delta\omega). \tag{135}$$

The boundary conditions for the dissociating system are given by the Møller operator Ω^-. Its effect on a plane wave is given by

$$\begin{aligned}
\Omega^-|\,\mathbf{k}\rangle &= \lim_{t\to\infty} e^{i\hat{H}_0 t/\hbar} e^{-i\hat{H}_{e,0} t/\hbar}|\,\mathbf{k}\rangle \\
&= \lim_{t\to\infty} e^{i(\hat{H}_0 - \hbar\omega_k)t/\hbar}|\,\mathbf{k}\rangle
\end{aligned} \tag{136}$$

We know that this limit exists, since at then end of times the system is dissociated, so that the excited state potential is zero, and $\hat{H}_0 = \hat{H}_{e,0}$. Using equation (72) we see that

$$\begin{aligned}
\lim_{t\to\infty} f(t) &= \lim_{t\to-\infty} f(-t) \\
&= \lim_{\epsilon\to 0^+} \int_{-\infty}^{0} \epsilon e^{\epsilon t} f(-t)\mathrm{d}t \\
&= \lim_{\epsilon\to 0^+} \int_{0}^{\infty} \epsilon e^{-\epsilon t} f(t)\mathrm{d}t \\
&= -\lim_{\epsilon\to 0^-} \int_{0}^{\infty} \epsilon e^{\epsilon t} f(t)\mathrm{d}t,
\end{aligned} \tag{137}$$

so that

$$\begin{aligned}
\Omega^-|\,\mathbf{k}\rangle &= -\lim_{\epsilon\to 0^-} \int_0^\infty \epsilon e^{i(\hat{H}_0 - \hbar\omega_k - i\hbar\epsilon)t/\hbar}|\,\mathbf{k}\rangle \\
&= \lim_{\epsilon\to 0^-} i\hbar\epsilon(\hat{H}_0 - \hbar\omega_k - i\hbar\epsilon)^{-1} e^{i(\hat{H}_0 - \hbar\omega_k - i\hbar\epsilon)t/\hbar}\Big|_0^\infty |\,\mathbf{k}\rangle \\
&= \lim_{\epsilon\to 0^-} i\hbar\epsilon(\hbar\omega_k + i\hbar\epsilon - \hat{H}_0)^{-1}|\,\mathbf{k}\rangle \\
&= \lim_{\epsilon\to 0^-} G(\hbar\omega_k + i\hbar\epsilon)|\,\mathbf{k}\rangle \\
&\equiv |\,\psi_{\mathbf{k}}^-\rangle.
\end{aligned} \tag{138}$$

Following equations (94) — (98), we see that we can write the representation of the wave function as

$$\langle\,\mathbf{r}|\,\psi_{\mathbf{k}}^-\rangle = \frac{1}{(2\pi)^{\frac{3}{2}}} e^{i\mathbf{k}\cdot\mathbf{r}} + \int \mathrm{d}\mathbf{r}' g_0^-(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi_{\mathbf{k}}^-(\mathbf{r}'). \tag{139}$$

The fact that the real energy axis is approached from the negative imaginary axis, in stead of from the positive imaginary axis as in the scattering problem, is reflected in the Green's function

$$g_0^-(\mathbf{r},\mathbf{r}') = -\frac{\mu}{2\pi\hbar^2|\mathbf{r}-\mathbf{r}'|} e^{-ik|\mathbf{r}-\mathbf{r}'|}, \tag{140}$$

which is the complex conjugate of $g_0^+(\mathbf{r},\mathbf{r}')$. Hence, in the Born approximation we get

$$\psi_{\mathbf{k}}^-(\mathbf{r}) = \frac{1}{(2\pi)^{\frac{3}{2}}} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\mu}{2\pi\hbar^2 r} e^{-ikr} \int \mathrm{d}\mathbf{r}' e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}'} V(\mathbf{r}'), \tag{141}$$

where $\mathbf{k}'$ is a vector of length k in the direction of $\mathbf{r}$, or in an alternative notation

$$\psi_{\mathbf{k}}^{-}(\mathbf{r}) = \frac{1}{(2\pi)^{\frac{3}{2}}} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{r} e^{-ikr} f(k, \hat{\mathbf{k}}, \hat{\mathbf{r}}). \tag{142}$$

We know that the kinetic energy of a plane wave, $E_k = \hbar\omega_k$, is given by

$$E_k = \frac{\hbar^2 k^2}{2\mu}, \tag{143}$$

so that the infinitesimal element

$$\mathrm{d}k = \frac{\mu}{\hbar^2 k} \mathrm{d}E_k. \tag{144}$$

Knowing that

$$\int \mathrm{d}\mathbf{k} |\, \mathbf{k} \rangle \langle\, \mathbf{k}\, | = \int k^2 \mathrm{d}k \mathrm{d}\hat{\mathbf{k}} |\, \mathbf{k} \rangle \langle\, \mathbf{k}\, | = \int \frac{\mu k}{\hbar^2} \mathrm{d}E_k \mathrm{d}\hat{\mathbf{k}} |\, \mathbf{k} \rangle \langle\, \mathbf{k}\, | = \hat{1}, \tag{145}$$

we define the energy normalized ket $|\, E_k \hat{\mathbf{k}} \rangle \equiv \sqrt{\mu k}/\hbar |\, \mathbf{k} \rangle$, for which

$$\int \mathrm{d}E_k \mathrm{d}\hat{\mathbf{k}} |\, E_k \hat{\mathbf{k}} \rangle \langle\, E_k \hat{\mathbf{k}}\, | = \hat{1}. \tag{146}$$

It easily seen then, that

$$|\, E_k \hat{\mathbf{k}} \rangle = \int \mathrm{d}E_{k'} \mathrm{d}\hat{\mathbf{k}}' |\, E_{k'} \hat{\mathbf{k}}' \rangle \langle\, E_{k'} \hat{\mathbf{k}}' |\, E_k \hat{\mathbf{k}} \rangle, \tag{147}$$

so that

$$\langle\, E_{k'} \hat{\mathbf{k}}' |\, E_k \hat{\mathbf{k}} \rangle = \delta(E_{k'} - E_k) \delta(\hat{\mathbf{k}}' - \hat{\mathbf{k}}). \tag{148}$$