Notes on Entropy Change Over Time

Duncan MacIntyre

January 9, 2024

Contents

1 Time-dependent perturbation theory

Suppose we have a Hamiltonian of the form

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

where $\hat{H}_0$ is a well-understood Hamiltonian that does not depend on time and $\hat{V}(t)$ is "small". For example, $\hat{H}_0$ might be the free particle Hamiltonian $\hat{H}_0 = \frac{m}{2}\nabla^2$. Our equation of motion is the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi, t\rangle = \Big(\hat{H}_0 + \hat{V}(t)\Big)|\Psi, t\rangle$$

where $|\Psi, t\rangle$ is the usual Schrödinger-picture state at time t.

Let $\hat{U}(t_0, t) = e^{-i\hat{H}_0(t-t_0)/\hbar}$. Then $\hat{U}(t_0, t)$ is the operator that evolves a state from time t_0 to time t according to $\hat{H}_0$. We define the interaction-picture state to be

$$|\Psi_I, t\rangle = \hat{U}(t_0, t)^\dagger |\Psi, t\rangle$$

so $|\Psi, t\rangle = \hat{U}(t_0, t)|\Psi_I, t\rangle$. Plugging this in to the Schrödinger equation,

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}\hat{U}(t_0, t)|\Psi_I, t\rangle &= \Big(\hat{H}_0 + \hat{V}(t)\Big)\hat{U}(t_0, t)|\Psi, t\rangle \\
i\hbar\left[\frac{\partial}{\partial t}e^{-i\hat{H}_0(t-t_0)/\hbar}\right]|\Psi_I, t\rangle + i\hbar e^{-i\hat{H}_0(t-t_0)/\hbar}\frac{\partial}{\partial t}|\Psi_I, t\rangle &= \hat{H}_0 e^{-i\hat{H}_0(t-t_0)/\hbar}|\Psi_I, t\rangle + \hat{V}(t)e^{-i\hat{H}_0(t-t_0)/\hbar}|\Psi_I, t\rangle \\
\cancel{-i^2\hat{H}_0 e^{i\hat{H}_0(t-t_0)/\hbar}|\Psi_I, t\rangle} + i\hbar e^{-i\hat{H}_0(t-t_0)/\hbar}\frac{\partial}{\partial t}|\Psi_I, t\rangle &= \cancel{\hat{H}_0 e^{-i\hat{H}_0(t-t_0)/\hbar}|\Psi_I, t\rangle} + \hat{V}(t)e^{-i\hat{H}_0(t-t_0)/\hbar}|\Psi_I, t\rangle \\
i\hbar\frac{\partial}{\partial t}|\Psi_I, t\rangle &= e^{i\hat{H}_0(t-t_0)/\hbar}\hat{V}(t)e^{-i\hat{H}_0(t-t_0)/\hbar}|\Psi_I, t\rangle \\
i\hbar\frac{\partial}{\partial t}|\Psi_I, t\rangle &= \hat{H}_I(t)|\Psi_I, t\rangle
\end{aligned}$$

where we define the interaction Hamiltonian to be

$$\hat{H}_I(t) = \hat{U}(t_0, t)^\dagger\hat{V}(t)\hat{U}(t_0, t) = e^{i\hat{H}_0(t-t_0)/\hbar}\hat{V}(t)e^{-i\hat{H}_0(t-t_0)/\hbar}.$$

This sets up the interaction picture. We have rephrased our problem so that we can continue with quantum mechanics normally without having to worry about the time evolution due to $\hat{H}_0$.

We now integrate both sides of our expression.

$$\begin{aligned}
\int_{t_0}^{t}\frac{\partial}{\partial t'}|\Psi_I, t'\rangle &= -\frac{i}{\hbar}\int_{t_0}^{t}\hat{H}_I(t')|\Psi_I, t'\rangle\, dt' \\
|\Psi_I, t\rangle - |\Psi_I, t_0\rangle &= -\frac{i}{\hbar}\int_{t_0}^{t}\hat{H}_I(t')|\Psi_I, t'\rangle\, dt' \\
|\Psi_I, t\rangle &= |\Psi_I, t_0\rangle - \frac{i}{\hbar}\int_{t_0}^{t}\hat{H}_I(t')|\Psi_I, t'\rangle\, dt' \qquad (1)
\end{aligned}$$

This is called the integral form of the Schrödinger equation.

We can now iteratively calculate perturbative approximations where we assume $\hat{H}_I(t)$ is small. The zero order approximation is simply

$$|\Psi_I, t\rangle = |\Psi_I, t_0\rangle + \mathcal{O}\Big(\hat{H}_I(t)\Big).$$

Plugging this in for the state inside the integral in (1), we get the first order approximation

$$|\Psi_I, t\rangle = |\Psi_I, t_0\rangle - \frac{i}{\hbar}\int_{t_0}^{t} \hat{H}_I(t')\,|\Psi_I, t_0\rangle\; dt' + \mathcal{O}\Big(\hat{H}_I(t)^2\Big). \tag{2}$$

Plugging this in to (1) again we get the second order approximation

$$\begin{aligned}|\Psi_I, t\rangle &= |\Psi_I, t_0\rangle - \frac{i}{\hbar}\int_{t_0}^{t} \hat{H}_I(t')\left[|\Psi_I, t_0\rangle - \frac{i}{\hbar}\int_{t_0}^{t'} \hat{H}_I(t'')\,|\Psi_I, t_0\rangle\; dt''\right] dt' + \mathcal{O}\Big(\hat{H}_I(t)^3\Big)\\ &= |\Psi_I, t_0\rangle - \frac{i}{\hbar}\int_{t_0}^{t} \hat{H}_I(t')\,|\Psi_I, t_0\rangle\; dt' - \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'} \hat{H}_I(t')\hat{H}_I(t'')\,|\Psi_I, t_0\rangle\; dt''\, dt' + \mathcal{O}\Big(\hat{H}_I(t)^3\Big).\end{aligned} \tag{3}$$

In general, we can keep going to achieve higher order approximations. For us, however, the second order approximation (3) is enough.

2 Time evolution of the density operator

We now consider mixed states. We will need to describe the system by the density operator $\hat{\rho}(t)$. Let's derive the time evolution of $\hat{\rho}(t)$ in second order perturbation theory based on (3).

Suppose at time t_0 we have a statistical ensemble of interaction-picture states $|\psi_{In}, t_0\rangle$ each with probability P_n. Then

$$\hat{\rho}(t_0) = \sum_n P_n\,|\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0|\,.$$

At time t states will have evolved according to (3), so

$$\hat{\rho}(t) = \sum_n P_n\,|\Psi_{In}, t\rangle\,\langle\Psi_{In}, t|\,.$$

From (3) we have

$$\begin{aligned}|\Psi_{In}, t\rangle &= |\Psi_I, t_0\rangle - \frac{i}{\hbar}\int_{t_0}^{t} \hat{H}_I(t')\,|\Psi_I, t_0\rangle\; dt' - \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'} \hat{H}_I(t')\hat{H}_I(t'')\,|\Psi_I, t_0\rangle\; dt''\, dt' + \mathcal{O}\Big(\hat{H}_I(t)^3\Big)\\ \langle\Psi_{In}, t| &= \langle\Psi_I, t_0| - \frac{i}{\hbar}\int_{t_0}^{t} \langle\Psi_I, t_0|\,\hat{H}_I(t')\, dt' - \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'} \langle\Psi_I, t_0|\,\hat{H}_I(t'')\hat{H}_I(t')\, dt''\, dt' + \mathcal{O}\Big(\hat{H}_I(t)^3\Big)\end{aligned}$$

so

$$\begin{aligned}|\Psi_{In}, t\rangle\,\langle\Psi_{In}, t| \;=\;& |\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0| \;-\; \frac{i}{\hbar}\int_{t_0}^{t}\Big(\hat{H}(t')\,|\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0| - |\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0|\,\hat{H}_I(t')\Big)\, dt'\\ &- \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'}\Big(\hat{H}_I(t')\hat{H}_I(t'')\,|\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0| + \;|\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0|\,\hat{H}_I(t'')\hat{H}_I(t')\Big)\, dt''\, dt'\\ &+ \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t}\hat{H}_I(t')\,|\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0|\,\hat{H}_I(t'')\, dt''\, dt'\\ =\;& |\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0| \;-\; \frac{i}{\hbar}\int_{t_0}^{t}\Big[\hat{H}(t'),\; |\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0|\Big]\, dt'\\ &- \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'}\Big\{\hat{H}_I(t')\hat{H}_I(t''),\; |\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0|\Big\}\, dt''\, dt'\\ &+ \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t}\hat{H}_I(t')\,|\Psi_{In}, t_0\rangle\,\langle\Psi_{In}, t_0|\,\hat{H}_I(t'')\, dt''\, dt'.\end{aligned}$$

Then

$$\begin{aligned}\hat{\rho}(t) \;&=\; \hat{\rho}\left(t_0\right) \;-\; \frac{i}{\hbar}\int_{t_0}^{t}\left[\hat{H}(t'),\; \hat{\rho}(t_0)\right] dt' \\ &\quad -\; \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'}\left\{\hat{H}_I(t')\hat{H}_I(t''),\; \hat{\rho}(t_0)\right\} dt''\, dt' \\ &\quad +\; \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t}\hat{H}_I(t')\hat{\rho}(t_0)\hat{H}_I(t'')\, dt''\, dt'.\end{aligned} \tag{4}$$

3 Eigenvalue corrections from perturbation theory

The goal of this section is to compute the second-order perturbative corrections to the eigenvalues of an operator. We use the approach known as time-independent perturbation theory.

Suppose $\hat{\rho}$ is an operator with eigenstates $|\Psi_n\rangle$ and eigenvalues σ_n. Suppose we have the asymptotic expansions

$$\begin{aligned}\hat{\rho} &= \hat{\rho}_0 + \lambda\hat{\rho}_1 + \lambda^2\hat{\rho}_2 + \mathcal{O}\big(\lambda^3\big) \\ |\Psi_n\rangle &= \left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \mathcal{O}\big(\lambda^3\big) \\ \sigma_n &= \sigma_n^{(0)} + \lambda\sigma_n^{(1)} + \lambda^2\sigma_n^{(2)} + \mathcal{O}\big(\lambda^3\big)\end{aligned}$$

where $\left\{\left|\Psi_n^{(0)}\right\rangle\right\}$ is an orthonormal basis for the Hilbert space.

We have $\hat{\rho}\,|\Psi_n\rangle = \sigma_n\,|\Psi_n\rangle$. In the zeroth order of λ this gives $\hat{\rho}_0\left|\Psi_n^{(0)}\right\rangle = \sigma_n^{(0)}\left|\Psi_n^{(0)}\right\rangle$, that is, $\left|\Psi_n^{(0)}\right\rangle$ is an eigenstate of $\hat{\rho}_0$ with eigenvalue $\sigma_n^{(0)}$.

Now, we have

$$\begin{aligned}\sigma_n\,|\Psi_n\rangle &= \hat{\rho}\,|\Psi_n\rangle \\ \left(\sigma_n^{(0)} - \sigma_m^{(0)} + \lambda\sigma_n^{(1)} + \lambda^2\sigma_n^{(2)} + \mathcal{O}\big(\lambda^3\big)\right)\left\langle\Psi_m^{(0)}|\Psi_n\right\rangle &= \left\langle\Psi_m^{(0)}\right|\lambda\hat{\rho}_1 + \lambda^2\hat{\rho}_2 + \mathcal{O}\big(\lambda^3\big)\,|\Psi_n\rangle \\ \left\langle\Psi_m^{(0)}|\Psi_n\right\rangle &= \frac{\left\langle\Psi_m^{(0)}\right|\lambda\hat{\rho}_1 + \lambda^2\hat{\rho}_2 + \mathcal{O}\big(\lambda^3\big)\,|\Psi_n\rangle}{\sigma_n^{(0)} - \sigma_m^{(0)} + \lambda\sigma_n^{(1)} + \lambda^2\sigma_n^{(2)} + \mathcal{O}(\lambda^3)}.\end{aligned}$$

We will next proceed to get rid of the denominator by using the Taylor expansion $\frac{1}{1+x} = 1 - x + \mathcal{O}\big(x^2\big)$.

Let D_n be the indices degenerate with n. That is, let $D_n = \{m : \sigma_m^{(0)} = \sigma_n^{(0)}\}$. Consider the case where $m \in D_n$. Let δ be a small real number. In the limit as $\delta \to 0$,

$$\begin{aligned}
\left\langle \Psi_m^{(0)} | \Psi_n \right\rangle &= \frac{\left\langle \Psi_m^{(0)} \right| \lambda\hat{\rho}_1 + \lambda^2\hat{\rho}_2 + \mathcal{O}\left(\lambda^3\right) \left|\Psi_n\right\rangle}{\lambda\sigma_n^{(1)} + \lambda^2\sigma_n^{(2)} + \mathcal{O}(\lambda^3) + \lambda\delta} \\
&= \frac{\left\langle \Psi_m^{(0)} \right| \lambda\hat{\rho}_1 + \lambda^2\hat{\rho}_2 + \mathcal{O}\left(\lambda^3\right) \left|\Psi_n\right\rangle}{\lambda\left(\sigma_n^{(1)} + \delta\right)\left(1 + \lambda\frac{\sigma_n^{(2)}}{\sigma_n^{(1)}+\delta} + \mathcal{O}(\lambda^2)\right)} \\
&= \frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 + \lambda\hat{\rho}_2 + \mathcal{O}\left(\lambda^2\right) \left|\Psi_n\right\rangle}{\sigma_n^{(1)} + \delta}\left(1 - \lambda\frac{\sigma_n^{(2)}}{\sigma_n^{(1)} + \delta} + \mathcal{O}\left(\lambda^2\right)\right) \\
&= \frac{\left\langle \Psi_m^{(0)} \right| \left(\hat{\rho}_1 + \lambda\hat{\rho}_2 + \mathcal{O}(\lambda^2)\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \mathcal{O}(\lambda^2)\right)}{\sigma_n^{(1)} + \delta}\left(1 - \lambda\frac{\sigma_n^{(2)}}{\sigma_n^{(1)} + \delta} + \mathcal{O}\left(\lambda^2\right)\right) \\
&= \frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left|\Psi_n^{(0)}\right\rangle}{\sigma_n^{(1)} + \delta} + \lambda\left[\frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_2 \left|\Psi_n^{(0)}\right\rangle}{\sigma_n^{(1)} + \delta} + \frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_2 \left|\Psi_n^{(1)}\right\rangle}{\sigma_n^{(1)} + \delta} - \frac{\sigma_n^{(2)}\left\langle \Psi_m^{(0)} \right| \hat{\rho}_2 \left|\Psi_n^{(0)}\right\rangle}{\left(\sigma_n^{(1)} + \delta\right)^2}\right] + \mathcal{O}\left(\lambda^2\right)
\end{aligned}$$

(The δ ensured that we did not divide by zero if $\sigma_n^{(1)} = 0$.) Now consider the case where $m \notin D_n$. Then

$$\begin{aligned}
\left\langle \Psi_m^{(0)} | \Psi_n \right\rangle &= \frac{\left\langle \Psi_m^{(0)} \right| \lambda\hat{\rho}_1 + \mathcal{O}\left(\lambda^2\right) \left|\Psi_n\right\rangle}{\left(\sigma_n^{(0)} - \sigma_m^{(0)}\right)(1 + \mathcal{O}(\lambda))} \\
&= \frac{\left\langle \Psi_m^{(0)} \right| \lambda\hat{\rho}_1 + \mathcal{O}\left(\lambda^2\right) \left|\Psi_n\right\rangle}{\sigma_n^{(0)} - \sigma_m^{(0)}}(1 + \mathcal{O}(\lambda)) \\
&= \lambda\frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left|\Psi_n\right\rangle}{\sigma_n^{(0)} - \sigma_m^{(0)}} + \mathcal{O}\left(\lambda^2\right).
\end{aligned}$$

Putting this all together,

$$\begin{aligned}
\left|\Psi_n\right\rangle &= \sum_{m\in D_n}\left|\Psi_m^{(0)}\right\rangle\left\langle \Psi_m^{(0)} | \Psi_n \right\rangle + \sum_{m\notin D_n}\left|\Psi_m^{(0)}\right\rangle\left\langle \Psi_m^{(0)} | \Psi_n \right\rangle \qquad (5) \\
&= \sum_{m\in D_n}\left|\Psi_m^{(0)}\right\rangle\lim_{\delta\to 0}\frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left|\Psi_n^{(0)}\right\rangle}{\sigma_n^{(1)} + \delta} \\
&\quad + \lambda\left(\sum_{m\in D_n}\left|\Psi_m^{(0)}\right\rangle\lim_{\delta\to 0}\left[\frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_2 \left|\Psi_n^{(0)}\right\rangle}{\sigma_n^{(1)} + \delta} + \frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left|\Psi_n^{(1)}\right\rangle}{\sigma_n^{(1)} + \delta} - \frac{\sigma_n^{(2)}\left\langle \Psi_m^{(0)} \right| \hat{\rho}_0 \left|\Psi_n^{(0)}\right\rangle}{\left(\sigma_n^{(1)} + \delta\right)^2}\right]\right. \\
&\qquad \left. + \sum_{m\notin D_n}\left|\Psi_m^{(0)}\right\rangle\frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left|\Psi_n\right\rangle}{\sigma_n^{(0)} - \sigma_m^{(0)}}\right) \\
&\quad + \mathcal{O}\left(\lambda^2\right)
\end{aligned}$$

In the zeroth order of λ, equation (5) gives

$$\left|\Psi_n^{(0)}\right\rangle = \sum_{m\in D_n}\left|\Psi_m^{(0)}\right\rangle\lim_{\delta\to 0}\frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left|\Psi_n^{(0)}\right\rangle}{\sigma_n^{(1)} + \delta}.$$

Multiplying by $\left\langle \Psi_n^{(0)} \right|$ we get

$$\boxed{\sigma_n^{(1)} = \left\langle \Psi_n^{(0)} \right| \hat{\rho}_1 \left| \Psi_n^{(0)} \right\rangle.} \tag{6}$$

If we instead multiply by $\left\langle \Psi_k^{(0)} \right|$ where $k \in D_n$ but $k \neq n$ we get

$$\boxed{0 = \left\langle \Psi_k^{(0)} \right| \hat{\rho}_1 \left| \Psi_n^{(0)} \right\rangle, \qquad k \in D_n, \qquad m \neq n.} \tag{7}$$

In other words, the matrix given by $\left\langle \Psi_k^{(0)} \right| \hat{\rho}_1 \left| \Psi_j^{(0)} \right\rangle$ is diagonal on $k, j \in D_n$, for any n.

In the first order of λ, equation (5) says

$$\left| \Psi_n^{(1)} \right\rangle = \sum_{m \in D_n} \left| \Psi_m^{(0)} \right\rangle \lim_{\delta \to 0} \left[\frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_2 \left| \Psi_n^{(0)} \right\rangle}{\sigma_n^{(1)} + \delta} + \frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left| \Psi_n^{(1)} \right\rangle}{\sigma_n^{(1)} + \delta} - \frac{\sigma_n^{(2)} \left\langle \Psi_m^{(0)} \right| \hat{\rho}_0 \left| \Psi_n^{(0)} \right\rangle}{\left(\sigma_n^{(1)} + \delta \right)^2} \right] + \sum_{m \notin D_n} \left| \Psi_m^{(0)} \right\rangle \frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left| \Psi_n \right\rangle}{\sigma_n^{(0)} - \sigma_m^{(0)}}.$$

Multiplying by $\left\langle \Psi_k^{(0)} \right|$ where $k \notin D_n$ gives

$$\left\langle \Psi_k^{(0)} | \Psi_n^{(1)} \right\rangle = \frac{\left\langle \Psi_k^{(0)} \right| \hat{\rho}_1 \left| \Psi_n^{(0)} \right\rangle}{\sigma_n^{(0)} - \sigma_k^{(0)}}.$$

If we instead multiply by $\left\langle \Psi_n^{(0)} \right|$ we get

$$0 = \left\langle \Psi_n^{(0)} | \Psi_n^{(1)} \right\rangle = \lim_{\delta \to 0} \left[\frac{\left\langle \Psi_n^{(0)} \right| \hat{\rho}_2 \left| \Psi_n^{(0)} \right\rangle}{\sigma_n^{(1)} + \delta} + \frac{\left\langle \Psi_n^{(0)} \right| \hat{\rho}_1 \left| \Psi_n^{(1)} \right\rangle}{\sigma_n^{(1)} + \delta} - \frac{\sigma_n^{(2)} \left(\sigma_n^{(1)} + \delta \right)}{\left(\sigma_n^{(1)} + \delta \right)^2} \right]$$

so

$$\begin{aligned}
\sigma_n^{(2)} &= \left\langle \Psi_n^{(0)} \right| \hat{\rho}_2 \left| \Psi_n^{(0)} \right\rangle + \left\langle \Psi_n^{(0)} \right| \hat{\rho}_1 \left| \Psi_n^{(1)} \right\rangle - \left\langle \Psi_n^{(0)} | \Psi_n^{(1)} \right\rangle \sigma_n^{(1)} \\
&= \left\langle \Psi_n^{(0)} \right| \hat{\rho}_2 \left| \Psi_n^{(0)} \right\rangle + \sum_{m \in D_n} \left\langle \Psi_n^{(0)} \right| \hat{\rho}_1 \left| \Psi_m^{(0)} \right\rangle \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle + \sum_{m \notin D_n} \left\langle \Psi_n^{(0)} \right| \hat{\rho}_1 \left| \Psi_m^{(0)} \right\rangle \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle - \left\langle \Psi_n^{(0)} | \Psi_n^{(1)} \right\rangle \sigma_n^{(1)} \\
&= \left\langle \Psi_n^{(0)} \right| \hat{\rho}_2 \left| \Psi_n^{(0)} \right\rangle + \sigma_n^{(1)} \left\langle \Psi_n^{(0)} | \Psi_n^{(1)} \right\rangle + \sum_{m \notin D_n} \left\langle \Psi_n^{(0)} \right| \hat{\rho}_1 \left| \Psi_m^{(0)} \right\rangle \frac{\left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left| \Psi_n^{(0)} \right\rangle}{\sigma_n^{(0)} - \sigma_m^{(0)}} - \left\langle \Psi_n^{(0)} | \Psi_n^{(1)} \right\rangle \sigma_n^{(1)}
\end{aligned}$$

hence

$$\boxed{\sigma_n^{(2)} = \left\langle \Psi_n^{(0)} \right| \hat{\rho}_2 \left| \Psi_n^{(0)} \right\rangle + \sum_{m \notin D_n} \frac{\left| \left\langle \Psi_m^{(0)} \right| \hat{\rho}_1 \left| \Psi_n^{(0)} \right\rangle \right|^2}{\sigma_n^{(0)} - \sigma_m^{(0)}}.} \tag{8}$$

4 The change in entropy

Both von Neumann and N-Tsallis entropy can be calculated from the eigenvalues of the density operator. We therefore study these eigenvalues with perturbation theory.

Suppose that, at some fixed time t, the density operator takes the form

$$\hat{\rho}(t) = \sum_n \sigma_n \left|\Psi_n\right\rangle \left\langle\Psi_n\right| \tag{9}$$

where $\left\{\left|\Psi_n^{(0)}\right\rangle\right\}$ is an orthonormal basis for the Hilbert space. Suppose we have asymptotic expansions

$$\begin{aligned}
\hat{\rho}(t) &= \hat{\rho}_0 + \lambda\hat{\rho}_1 + \lambda^2\hat{\rho}_2 + \mathcal{O}\big(\lambda^3\big) \\
\left|\Psi_n\right\rangle &= \left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \mathcal{O}\big(\lambda^3\big) \\
\sigma_n &= \sigma_n^{(0)} + \lambda\sigma_n^{(1)} + \lambda^2\sigma_n^{(2)} + \mathcal{O}\big(\lambda^3\big)
\end{aligned}$$

The above is indeed true if we take λ to be proportional to $\hat{H}_I(t)$ and take

$$\hat{\rho}_0 = \hat{\rho}\left(t_0\right) \tag{10}$$

$$\hat{\rho}_1 = -\frac{i}{\hbar}\int_{t_0}^{t} \left[\hat{H}(t'),\ \hat{\rho}_0\right] dt' \tag{11}$$

$$\hat{\rho}_2 = -\frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'} \left\{\hat{H}_I(t')\hat{H}_I(t''),\ \hat{\rho}_0\right\} dt''\,dt' + \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t} \hat{H}_I(t')\,\hat{\rho}_0\,\hat{H}_I(t'')\,dt''\,dt'. \tag{12}$$

as per equation (4).

4(a) The first-order correction vanishes

Combining (6) and (11), the first-order eigenvalue correction is

$$\sigma_n^{(1)} = -\frac{i}{\hbar}\int_{t_0}^{t} \left\langle\Psi_n^{(0)}\right| \left[\hat{H}(t'),\ \hat{\rho}_0\right] \left|\Psi_n^{(0)}\right\rangle dt'.$$

Since

$$\left\langle\Psi_n^{(0)}\right| \hat{H}(t')\hat{\rho}_0 \left|\Psi_n^{(0)}\right\rangle = \sigma_n^{(0)} \left\langle\Psi_n^{(0)}\right| \hat{H}(t') \left|\Psi_n^{(0)}\right\rangle = \left\langle\Psi_n^{(0)}\right| \hat{\rho}_0\hat{H}(t') \left|\Psi_n^{(0)}\right\rangle$$

we have $\sigma_n^{(1)} = 0$.

4(b) Von Neumann entropy

The Von Neumann entropy for the state (9) is defined to be

$$S = \sum_n \sigma_n \log\sigma_n.$$

Let $A = \{n : \sigma_n^{(0)} \neq 0\}$. Then

$$\begin{aligned}
S &= -\sum_{n\in A}\sigma_n\log\sigma_n - \sum_{n\notin A}\sigma_n\log\sigma_n \\
&= -\sum_{n\in A}\sigma_n\log\left(\sigma_n^{(0)}\left(1+\mathcal{O}\big(\lambda^2\big)\right)\right) - \sum_{n\notin A}\sigma_n\log\left(\lambda^2\sigma_n^{(2)}\left(1+\mathcal{O}(\lambda)\right)\right) \\
&= -\sum_{n\in A}\left(\sigma_n^{(0)}+\mathcal{O}\big(\lambda^2\big)\right)\left(\log\sigma_n^{(0)}+\mathcal{O}\big(\lambda^2\big)\right) - \sum_{n\notin A}\sigma_n\left(\log\lambda^2+\log\sigma_n^{(2)}+\mathcal{O}(\lambda)\right) \\
&= -\sum_{n\in A}\sigma_n^{(0)}\log\sigma_n^{(0)} - \sum_{n\notin A}\sigma_n\log\lambda^2 + \mathcal{O}\big(\lambda^2\big).
\end{aligned}$$

The first term is

$$S_0 = -\sum_{n\in A} \sigma_n^{(0)} \log \sigma_n^{(0)}$$

which is the von Neumann entropy associated with the unperturbed density operator $\hat{\rho}_0 = \hat{\rho}\,(t_0)$. Thus the change in entropy due to the interaction is

$$\Delta S = S - S_0 = \log \frac{1}{\lambda^2} \sum_{n\notin A} \sigma_n + \mathcal{O}(\lambda^2) = \lambda^2 \log \frac{1}{\lambda^2} \sum_{n\notin A} \sigma_n^{(2)} + \mathcal{O}(\lambda^2). \tag{13}$$

Each σ_n is non-negative because it is an eigenvalue of a density operator; thus the entire change in entropy is non-negative to the leading order (assuming this term does not vanish).

We can recognize that $\sum_{n\in A} \sigma_n + \sum_{n\notin A} \sigma_n = 1$ and so

$$\Delta S = \left(1 - \sum_{n\in A} \left[\sigma_n^{(0)} + \lambda^2 \sigma_n^{(2)}\right]\right) \log \frac{1}{\lambda^2} + \mathcal{O}(\lambda^2)$$

and, since $\sum_{n\in A} \sigma_n^{(0)} = 1$,

$$\Delta S = -\lambda^2 \log \frac{1}{\lambda^2} \sum_{n\in A} \sigma_n^{(2)} + \mathcal{O}(\lambda^2). \tag{14}$$

Substituting in (8),

$$\Delta S = -\lambda^2 \log \frac{1}{\lambda^2} \left(\sum_{n\in A} \left\langle \Psi_n^{(0)} \middle| \hat{\rho}_2 \middle| \Psi_n^{(0)} \right\rangle + \sum_{n\in A} \sum_{m\notin D_n} \frac{\left| \left\langle \Psi_m^{(0)} \middle| \hat{\rho}_1 \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\sigma_n^{(0)} - \sigma_m^{(0)}} \right) + \mathcal{O}(\lambda^2).$$

Now, in the second term with the double sum, for every term $\frac{\left| \left\langle \Psi_m^{(0)} \middle| \hat{\rho}_1 \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\sigma_n^{(0)} - \sigma_m^{(0)}}$ there is an equal but opposite term $\frac{\left| \left\langle \Psi_m^{(0)} \middle| \hat{\rho}_1 \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\sigma_m^{(0)} - \sigma_n^{(0)}}$. Thus this double sum evaluates to zero. We end up with

$$\boxed{\Delta S = -\lambda^2 \log \frac{1}{\lambda^2} \sum_{n\in A} \left\langle \Psi_n^{(0)} \middle| \hat{\rho}_2 \middle| \Psi_n^{(0)} \right\rangle + \mathcal{O}(\lambda^2).} \tag{15}$$

Substituting in (12) and using that

$$\left\langle \Psi_n^{(0)} \middle| \left\{ \hat{H}_I(t') \hat{H}_I(t''),\ \hat{\rho}_0 \right\} \middle| \Psi_n^{(0)} \right\rangle = 2\sigma_n^{(0)} \left\langle \Psi_n^{(0)} \middle| \hat{H}_I(t') \hat{H}_I(t'') \middle| \Psi_n^{(0)} \right\rangle$$

we get

$$\begin{aligned} \Delta S = \frac{1}{\hbar^2} \lambda^2 \log \frac{1}{\lambda^2} \sum_{n\in A} \Bigg(& 2\sigma_n^{(0)} \int_{t_0}^{t} \int_{t_0}^{t'} \left\langle \Psi_n^{(0)} \middle| \hat{H}_I(t') \hat{H}_I(t'') \middle| \Psi_n^{(0)} \right\rangle dt''\, dt' \\ & - \int_{t_0}^{t} \int_{t_0}^{t} \left\langle \Psi_n^{(0)} \middle| \hat{H}_I(t')\, \hat{\rho}_0\, \hat{H}_I(t'') \middle| \Psi_n^{(0)} \right\rangle dt''\, dt' \Bigg) + \mathcal{O}(\lambda^2). \end{aligned} \tag{16}$$

4(c) N-Tsallis entropy

(to be added)

Appendices

These are extra calculations that are not relevant to the above discussion. They should be removed from documents to be shared. (I don't delete them now because they could be useful in future work.)

A The first-order approximation for pure states in scattering

We will continue for scattering between two particles. We will assume that the particles are distinguishable so that we don't need to restrict ourselves to symmetric or antisymmetric states. We will also assume that the particles interact in a way that only depends on the distance between them. That is, in the position basis, we can write

$$\langle x_1, x_2| \hat{V}(t) |\psi\rangle = \int_{x_1,x_2} d^3x_1\, d^3x_2\; V(x_1 - x_2) \langle x_1, x_2|\psi\rangle \,. \tag{17}$$

(Note that this is not time dependent.) Take $\hat{H}_0$ to be the free particle Hamiltonian.

It will be easiest to work in the momentum basis. We will do our calculations for momentum eigenstates—that is, plane waves. Write momentum eigenstates as $|k_1, k_2\rangle$. In the position basis these have wavefunctions

$$\langle x_1, x_2|k_1, k_2\rangle = \frac{1}{(2\pi)^3}\; e^{ik_1\cdot x_1 + ik_2\cdot x_2}. \tag{18}$$

Here x_1 and x_2 are the (3-vector) positions of the first and second particles and k_1 and k_2 are the (3-vector) momenta of the first and second particle. Also, we note that $|k_1, k_2\rangle$ has energy $\frac{1}{2m_1}{k_1}^2 + \frac{1}{2m_2}{k_2}^2$ and so

$$\hat{U}(t_0, t) |k_1, k_2\rangle = e^{-\frac{i}{\hbar}(t-t_0)\left(\frac{1}{2m_1}{k_1}^2 + \frac{1}{2m_2}{k_2}^2\right)} |k_1, k_2\rangle \,. \tag{19}$$

Let $\widetilde{V}(p)$ be the Fourier transform of $V(x_1 - x_2)$ so that

$$V(x_1 - x_2) = \int_{-\infty}^{\infty} \frac{d^3p}{(2\pi)^3} \widetilde{V}(p) e^{ip\cdot(x_1 - x_2)}. \tag{20}$$

We now consider (2) and take the limits $t_0 \to -\infty$ and $t \to \infty$ because, in scattering, we measure states long before and long after the scattering occurs. Then, dropping the higher-order terms,

$$|\Psi_I, \infty\rangle = |\Psi_I, -\infty\rangle - \frac{i}{\hbar}\int_{-\infty}^{\infty} \hat{H}_I(t) |\Psi_I, -\infty\rangle \; dt.$$

Take the initial state to be $|\Psi_I, -\infty\rangle = |k_1, k_2\rangle$. Multiplying by the bra $\langle k_1', k_2'|$,

$$\begin{aligned}\left\langle k_1', k_2'|\Psi_I, \infty\right\rangle &= \left\langle k_1', k_2'|k_1, k_2\right\rangle - \frac{i}{\hbar}\int_{-\infty}^{\infty} \left\langle k_1', k_2'\right| \hat{H}_I(t) |k_1, k_2\rangle \; dt \\ &= \delta^3(k_1' - k_1)\delta^3(k_2' - k_2) - \frac{i}{\hbar}\int_{-\infty}^{\infty} \left\langle k_1', k_2'\right| \hat{H}_I(t) |k_1, k_2\rangle \; dt.\end{aligned} \tag{21}$$

This motivates us to compute the matrix element $\langle k_1', k_2'| \hat{H}_I(t) |k_1, k_2\rangle$. We can start by using (19):

$$
\begin{aligned}
\left\langle k_1', k_2'\right| \hat{H}_I(t) \left|k_1, k_2\right\rangle &= \left\langle k_1', k_2'\right| \hat{U}(t_0, t)^\dagger \hat{V}(t) \hat{U}(t_0, t) \left|k_1, k_2\right\rangle \\
&= \left\langle k_1', k_2'\right| e^{\frac{i}{\hbar}(t-t_0)\left(\frac{1}{2m_1}{k_1'}^2 + \frac{1}{2m_2}{k_2'}^2\right)} \hat{V}(t) e^{-\frac{i}{\hbar}(t-t_0)\left(\frac{1}{2m_1}{k_1}^2 + \frac{1}{2m_2}{k_2}^2\right)} \left|k_1, k_2\right\rangle \\
&= e^{-\frac{i}{\hbar}(t-t_0)\left(\frac{1}{2m_1}{k_1'}^2 + \frac{1}{2m_2}{k_2'}^2 - \frac{1}{2m_1}{k_1}^2 - \frac{1}{2m_2}{k_2}^2\right)} \left\langle k_1', k_2'\right| \hat{V}(t) \left|k_1, k_2\right\rangle .
\end{aligned}
$$

We see that

$$
\begin{aligned}
\left\langle k_1', k_2'\right| \hat{V}(t) \left|k_1, k_2\right\rangle &= \left\langle k_1', k_2'\right| \left\{ \int_{x_1, x_2} d^3x_1 d^3x_2 \; \left|x_1, x_2\right\rangle \left\langle x_1, x_2\right| \right\} \hat{V}(t) \left|k_1, k_2\right\rangle \\
&= \int_{x_1, x_2} d^3x_1 d^3x_2 \; \left\langle k_1', k_2' | x_1, x_2\right\rangle \left\langle x_1, x_2\right| \hat{V}(t) \left|k_1, k_2\right\rangle \\
&= \int_{x_1, x_2} \frac{d^3x_1 d^3x_2}{(2\pi)^6} \; e^{-ik_1'\cdot x_1 - ik_2'\cdot x_2} V(x_1 - x_2) e^{ik_1\cdot x_1 + ik_2\cdot x_2} \qquad \text{(by (17) and (18))} \\
&= \int_{-\infty}^{\infty} \frac{d^3p}{(2\pi)^9} \int_{x_1, x_2} d^3x_1 d^3x_2 \;\; e^{-ik_1'\cdot x_1 - ik_2'\cdot x_2} \, \widetilde{V}(p) \, e^{ip\cdot(x_1 - x_2)} e^{ik_1\cdot x_1 + ik_2\cdot x_2} \qquad \text{(by (20))} \\
&= \int_{-\infty}^{\infty} \frac{d^3p}{(2\pi)^9} \widetilde{V}(p) \int_{x_1, x_2} d^3x_1 d^3x_2 \;\; e^{i(k_1 - k_1' + p)\cdot x_1} e^{i(k_2 - k_2' - p)\cdot x_2} \\
&= \int_{-\infty}^{\infty} \frac{d^3p}{(2\pi)^9} \widetilde{V}(p) \, (2\pi)^6 \, \delta^3(k_1 - k_1' + p) \, \delta^3(k_2 - k_2' - p) \\
&= \frac{1}{(2\pi)^3} \, \widetilde{V}(k_1' - k_1) \; \delta^3(k_1' - k_1 - k_2' + k_2).
\end{aligned}
$$

so

$$
\left\langle k_1', k_2'\right| \hat{H}_I(t) \left|k_1, k_2\right\rangle = e^{-\frac{i}{\hbar}(t-t_0)\left(\frac{1}{2m_1}{k_1'}^2 + \frac{1}{2m_2}{k_2'}^2 - \frac{1}{2m_1}{k_1}^2 - \frac{1}{2m_2}{k_2}^2\right)} \frac{1}{(2\pi)^3} \, \widetilde{V}(k_1' - k_1) \; \delta^3(k_1' - k_1 - k_2' + k_2)
$$

If we integrate over all time, we get a delta function:

$$
\int_{-\infty}^{\infty} dt \; \left\langle k_1', k_2'\right| \hat{H}_I(t) \left|k_1, k_2\right\rangle = \frac{\hbar}{(2\pi)^2} \, \widetilde{V}(k_1' - k_1) \, \delta\left(\tfrac{1}{2m_1}{k_1'}^2 + \tfrac{1}{2m_2}{k_2'}^2 - \tfrac{1}{2m_1}{k_1}^2 - \tfrac{1}{2m_2}{k_2}^2\right) \delta^3(k_1' - k_1 - k_2' + k_2). \tag{22}
$$

Putting this into (21),

$$
\begin{aligned}
\left\langle k_1', k_2' | \Psi_I, \infty\right\rangle = \; & \delta^3(k_1' - k_1) \, \delta^3(k_2' - k_2) \\
& - \frac{i}{(2\pi)^2} \, \widetilde{V}(k_1' - k_1) \; \delta^3(k_1' - k_1 - k_2' + k_2) \; \delta\left(\frac{{k_1'}^2}{2m_1} + \frac{{k_2'}^2}{2m_2} - \frac{{k_1}^2}{2m_1} - \frac{{k_2}^2}{2m_2} \right).
\end{aligned} \tag{23}
$$

Interestingly, we see that the delta functions cause energy and momentum to be conserved.

B Reduced density operator

We are interested in the situation where the second particle exits the system and becomes lost. We therefore consider the reduced density operator

$$
\begin{aligned}
\hat{\rho}_{\text{reduced}}(t) &= \int d^3k_2 \, \left\langle k_2\right| \hat{\rho}(t) \left|k_2\right\rangle \\
&= \hat{\rho}_{\text{reduced}}(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} dt' \int_{-\infty}^{\infty} d^3k_2 \, \left\langle k_2\right| \left[\hat{H}_I(t'), \; \hat{\rho}(t_0)\right] \left|k_2\right\rangle + \mathcal{O}\Big(\hat{H}_I(t)^2\Big).
\end{aligned}
$$

In the momentum basis the matrix elements are

$$\left\langle k_1'\right| \hat{\rho}_{\text{reduced}}(t)\left|k_1\right\rangle = \left\langle k_1'\right| \hat{\rho}_{\text{reduced}}\left(t_0\right)\left|k_1\right\rangle - \frac{i}{\hbar}\int_{t_0}^{t} dt' \int_{-\infty}^{\infty} d^3k_2 \left\langle k_1', k_2\right| \left[\hat{H}_I(t'),\ \hat{\rho}\left(t_0\right)\right] \left|k_1, k_2\right\rangle + \mathcal{O}\left(\hat{H}_I(t)^2\right).$$

As before, we drop the higher order terms and take $t \to \infty$ and $t_0 \to -\infty$. Then

$$\begin{aligned}
\left\langle k_1{}'\right| \hat{\rho}_{\text{reduced}}(\infty)\left|k_1\right\rangle &= \left\langle k_1'\right| \hat{\rho}_{\text{reduced}}\left(-\infty\right)\left|k_1\right\rangle - \frac{i}{\hbar}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} d^3k_2 \left\langle k_1', k_2\right| \left[\hat{H}_I(t),\ \hat{\rho}\left(-\infty\right)\right] \left|k_1, k_2\right\rangle \\
&= \left\langle k_1'\right| \hat{\rho}_{\text{reduced}}\left(-\infty\right)\left|k_1\right\rangle \\
&\quad - \frac{i}{\hbar}\int_{-\infty}^{\infty} d^3k_2\, d^3\widetilde{k}_1\, d^3\widetilde{k}_2 \left\{\int_{-\infty}^{\infty} dt \left\langle k_1', k_2\right| \hat{H}_I(t) \left|\widetilde{k}_1, \widetilde{k}_2\right\rangle\right\} \left\langle \widetilde{k}_1, \widetilde{k}_2\right| \hat{\rho}\left(-\infty\right)\left|k_1, k_2\right\rangle \\
&\quad + \frac{i}{\hbar}\int_{-\infty}^{\infty} d^3k_2\, d^3\widetilde{k}_1\, d^3\widetilde{k}_2 \left\langle k_1', k_2\right| \hat{\rho}\left(-\infty\right)\left|\widetilde{k}_1, \widetilde{k}_2\right\rangle \left\{\int_{-\infty}^{\infty} dt \left\langle \widetilde{k}_1, \widetilde{k}_2\right| \hat{H}_I(t) \left|k_1, k_2\right\rangle\right\}.
\end{aligned}$$

Plugging in our result (22),

$$\begin{aligned}
\left\langle k_1{}'\right| \hat{\rho}_{\text{reduced}}(\infty)\left|k_1\right\rangle &= \left\langle k_1'\right| \hat{\rho}_{\text{reduced}}\left(-\infty\right)\left|k_1\right\rangle \\
&\quad - i\int_{-\infty}^{\infty} d^3k_2\, d^3\widetilde{k}_1\, d^3\widetilde{k}_2 \left(\frac{1}{(2\pi)^2}\ \widetilde{V}\left(k_1' - \widetilde{k}_1\right)\ \delta\left(\tfrac{k_1'^{\,2}}{2m_1} + \tfrac{k_2{}^2}{2m_2} - \tfrac{\widetilde{k}_1^2}{2m_1} - \tfrac{\widetilde{k}_2^2}{2m_2}\right)\right. \\
&\qquad \left. \delta^3(k_1' - \widetilde{k}_1 - k_2 + \widetilde{k}_2)\ \left\langle \widetilde{k}_1, \widetilde{k}_2\right| \hat{\rho}\left(-\infty\right)\left|k_1, k_2\right\rangle\right) \\
&\quad + i\int_{-\infty}^{\infty} d^3k_2\, d^3\widetilde{k}_1\, d^3\widetilde{k}_2 \left(\frac{1}{(2\pi)^2}\ \widetilde{V}\left(\widetilde{k}_1 - k_1\right)\ \delta\left(\tfrac{\widetilde{k}_1^2}{2m_1} + \tfrac{\widetilde{k}_2^2}{2m_2} - \tfrac{k_1{}^2}{2m_1} - \tfrac{k_2{}^2}{2m_2}\right)\right. \\
&\qquad \left. \delta^3(\widetilde{k}_1 - k_1 - \widetilde{k}_2 + k_2)\ \left\langle k_1', k_2\right| \hat{\rho}\left(-\infty\right)\left|\widetilde{k}_1, \widetilde{k}_2\right\rangle\right).
\end{aligned}$$

Finally, we use the delta functions to get rid of the $\widetilde{k}_1$ integrals. This gives us

$$\begin{aligned}
\left\langle k_1{}'\right| \hat{\rho}_{\text{reduced}}(\infty)\left|k_1\right\rangle &= \left\langle k_1'\right|\hat{\rho}_{\text{reduced}}\left(-\infty\right)\left|k_1\right\rangle \\
&\quad - i\int_{-\infty}^{\infty} d^3k_2\, d^3\widetilde{k}_2\ \frac{1}{(2\pi)^2}\ \widetilde{V}\left(k_2 - \widetilde{k}_2\right)\ \left\langle k_1' + \widetilde{k}_2 - k_2,\ \widetilde{k}_2\right| \hat{\rho}\left(-\infty\right)\left|k_1, k_2\right\rangle\ D(k_1', k_2, \widetilde{k}_2) \\
&\quad + i\int_{-\infty}^{\infty} d^3k_2\, d^3\widetilde{k}_2\ \frac{1}{(2\pi)^2}\ \widetilde{V}\left(\widetilde{k}_2 - k_2\right)\ \left\langle k_1', k_2\right| \hat{\rho}\left(-\infty\right)\left|k_1 + \widetilde{k}_2 - k_2,\ \widetilde{k}_2\right\rangle\ D(k_1, k_2, \widetilde{k}_2).
\end{aligned}$$

where

$$D(k_1, k_2, \widetilde{k}_2) = \delta\left(\tfrac{1}{2}\ k_2{}^2\left(\tfrac{1}{m_1} - \tfrac{1}{m_2}\right) + \tfrac{1}{2}\ \widetilde{k}_2^2\left(\tfrac{1}{m_1} + \tfrac{1}{m_2}\right) - \tfrac{1}{2m_1}\left(-k_1\cdot\widetilde{k}_2 + k_1\cdot k_2 + \widetilde{k}_2\cdot k_2\right)\right).$$

Then, assuming $\widetilde{V}$ is an even function,

$$\begin{aligned}
\left\langle k_1{}'\right|\hat{\rho}_{\text{reduced}}(\infty)\left|k_1\right\rangle = \Bigg(&\left\langle k_1'\right| \hat{\rho}_{\text{reduced}}\left(-\infty\right)\left|k_1\right\rangle\ + \\
&\int_{-\infty}^{\infty} \frac{d^3k_2\, d^3\widetilde{k}_2}{(2\pi)^2}\ \widetilde{V}\left(k_2 - \widetilde{k}_2\right)\ \left(P\left(k_1, k_1'k_2, \widetilde{k}_2\right) D\left(k_1, k_2, \widetilde{k}_2\right) + P^*\left(k_1', k_1, k_2, \widetilde{k}_2\right) D\left(k_1', k_2, \widetilde{k}_2\right)\right)\Bigg)
\end{aligned} \tag{24}$$

where

$$P(k_1, k_1', k_2, \widetilde{k}_2) = i\left\langle k_1', k_2\right| \hat{\rho}\left(-\infty\right)\left|k_1 + \widetilde{k}_2 - k_2,\ \widetilde{k}_2\right\rangle.$$