# Tutorial: Perturbation Approximations to Asymptotic Quantum Transition Rates 

Steven Kenneth Kauffmann*


#### Abstract

The orders of the perturbation approximation to the Schrödinger-picture time evolution operator in powers of the presumed-small perturbation part of the Hamiltonian operator are developed by the iteration of an identity; the possibly confusing switch to the "interaction picture" isn't needed. Those time-evolution operator approximations are sandwiched between two orthogonal, normalized eigenstates of the "unperturbed" part of the Hamiltonian operator to produce the transition amplitude approximations, whose calculation is reduced to quadrature when every occurrence of the perturbation part of the Hamiltonian operator in them is expanded in the "unperturbed" basis. That expansion also reveals the time-dependent parts of those approximations to be multiply nested integrals which in the long-time limit approach simple products of non-singular inverses (principle value plus delta function) of differences of "unperturbed" energy eigenvalues. Closely related to the long-time limits of transition amplitudes are the long-time averages of transition rates. When the "unperturbed" basis is that of free-particle states, sums over relevant final states of transition rates from an initial state, divided by the initial state's particle flux, produce cross sections. Here the perturbation approximations to generic quantum transition rates are parlayed to the corresponding approximations to differential cross sections for nonrelativistic-particle potential scattering.


## Introduction

Given a Hamiltonian operator $\widehat{H}$ of the form $\widehat{H}=\widehat{H}_{0}+\widehat{V}$, where all of the eigenvectors $\psi_{j}^{(0)}$ and corresponding eigenvalues $E_{j}^{(0)}$ of the "unperturbed" Hamiltonian operator $\widehat{H}_{0}$ are known in analytic form, and where the additional operator term $\widehat{V}$ is a small perturbation of $\widehat{H}_{0}$, the time-dependent transition amplitudes,

$$
\begin{equation*}
\left(\psi_{l}^{(0)}, e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar} \psi_{i}^{(0)}\right) \text { where }\left(\psi_{l}^{(0)}, \psi_{i}^{(0)}\right)=0 \tag{1}
\end{equation*}
$$

can be reduced to quadrature when they are calculated to only a finite order in the small perturbation $\widehat{V}$.
To show in detail the reductions to quadrature of the perturbation approximations to finite orders in $\widehat{V}$ of the Eq. (1) time-dependent transition amplitudes, we need to work out the expansion in orders of $\widehat{V}$ of the crucial time-evolution operator $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ which is present in Eq. (1). If it should happen that the operators $\widehat{H}_{0}$ and $\widehat{V}$ commute, expanding $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ in orders of $\widehat{V}$ is straightforward,

$$
\begin{gather*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}=e^{-i\left(\widehat{H}_{0}+\widehat{V}\right)\left(t-t_{0}\right) / \hbar}=e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar} e^{-i \widehat{V}\left(t-t_{0}\right) / \hbar}= \\
e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \widehat{V}\left(t-t_{0}\right)+\sum_{k=2}^{\infty}(-i / \hbar)^{k}(\widehat{V})^{k}\left(t-t_{0}\right)^{k} / k!\right) . \tag{2}
\end{gather*}
$$

When the operators $\widehat{H}_{0}$ and $\widehat{V}$ don't commute, the expansion in orders of $\widehat{V}$ of $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ will of course be much more complicated than the Eq. (2) result, but its form can still be expected to have recognizable similarities to Eq. (2). Motivated by the form of Eq. (2), we write,

$$
\begin{equation*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}=e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(e^{+i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar} e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}\right) \tag{3a}
\end{equation*}
$$

We now note that,

$$
\begin{gather*}
d\left(e^{+i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar} e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}\right) / d t=(-i / \hbar)\left(e^{+i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(-\widehat{H}_{0}+\widehat{H}\right) e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}\right)=  \tag{3b}\\
(-i / \hbar)\left(e^{+i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}\right),
\end{gather*}
$$

and we also note that,

$$
\begin{equation*}
\left(e^{+i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar} e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}\right)_{t=t_{0}}=\widehat{I} \tag{3c}
\end{equation*}
$$

*Retired, American Physical Society Senior Life Member, E-mail: SKKauffmann@gmail.com

Eqs. (3b) and (3c) together imply that,

$$
\begin{equation*}
\left(e^{+i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar} e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}\right)=\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}\left(t^{(1)}-t_{0}\right) / \hbar}\right) \tag{3d}
\end{equation*}
$$

Eqs. (3a) and (3d) yield that the time evolution operator $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ satisfies the identity,

$$
\begin{equation*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}=e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}\left(t^{(1)}-t_{0}\right) / \hbar}\right) \tag{3e}
\end{equation*}
$$

Inserting the Eq. (3e) identity for $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ into itself yields the more elaborate identity,

$$
\begin{gather*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}=e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}+\right. \\
\left.(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}(-i / \hbar) \int_{t_{0}}^{t^{(1)}} d t^{(2)} e^{+i \widehat{H}_{0}\left(t^{(2)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}\left(t^{(2)}-t_{0}\right) / \hbar}\right), \tag{3f}
\end{gather*}
$$

which shows that the first-order in $\widehat{V}$ perturbation approximation to $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ is,

$$
\begin{equation*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}=e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}+O\left(\widehat{V}^{2}\right)\right) \tag{3g}
\end{equation*}
$$

Inserting the Eq. (3e) identity for $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ into its Eq. (3f) identity yields the yet more elaborate,

$$
\begin{gather*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}=e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}+\right. \\
(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}(-i / \hbar) \int_{t_{0}}^{t^{(1)}} d t^{(2)} e^{+i \widehat{H}_{0}\left(t^{(2)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(2)}-t_{0}\right) / \hbar}+ \\
(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}(-i / \hbar) \int_{t_{0}}^{t^{(1)}} d t^{(2)} e^{+i \widehat{H}_{0}\left(t^{(2)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(2)}-t_{0}\right) / \hbar} \times  \tag{3h}\\
\left.(-i / \hbar) \int_{t_{0}}^{t^{(2)}} d t^{(3)} e^{+i \widehat{H}_{0}\left(t^{(3)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}\left(t^{(3)}-t_{0}\right) / \hbar}\right)
\end{gather*}
$$

which shows that the second-order in $\widehat{V}$ perturbation approximation to $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ is,

$$
\begin{gather*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}=e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}+(-i / \hbar) \times\right. \\
\left.\int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}(-i / \hbar) \int_{t_{0}}^{t^{(1)}} d t^{(2)} e^{+i \widehat{H}_{0}\left(t^{(2)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(2)}-t_{0}\right) / \hbar}+O\left(\widehat{V}^{3}\right)\right) . \tag{3i}
\end{gather*}
$$

Continuing in this way can be proved by induction to, for $n=2,3,4, \ldots$, generate the sequence of identities,

$$
\begin{gather*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}=e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}+\sum_{k=2}^{n}[(-i / \hbar) \times\right. \\
\left.\int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \cdots(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i \widehat{H}_{0}\left(t^{(k)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(k)}-t_{0}\right) / \hbar}\right] \\
\quad+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \cdots(-i / \hbar) \int_{t_{0}}^{t^{(n-1)}} d t^{(n)} \times  \tag{3j}\\
\left.e^{+i \widehat{H}_{0}\left(t^{(n)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(n)}-t_{0}\right) / \hbar}(-i / \hbar) \int_{t_{0}}^{t^{(n)}} d t^{(n+1)} e^{+i \widehat{H}_{0}\left(t^{(n+1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}\left(t^{(n+1)}-t_{0}\right) / \hbar}\right)
\end{gather*}
$$

which shows that the $n$ th-order in $\widehat{V}$ perturbation approximation to $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ is,

$$
\begin{align*}
& e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}= e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}+\right. \\
& \sum_{k=2}^{n}\left[(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \cdots\right.  \tag{3k}\\
&\left.\left.(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i \widehat{H}_{0}\left(t^{(k)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(k)}-t_{0}\right) / \hbar}\right]+O\left(\widehat{V}^{n+1}\right)\right)
\end{align*}
$$

Eqs. (3j) and (3k) suggest that $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ may have the formal perturbation series representation,

$$
\begin{align*}
e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar}= & e^{-i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar}\left(\widehat{I}+(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar}+\right. \\
& \sum_{k=2}^{\infty}\left[(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \ldots\right.  \tag{31}\\
& \left.\left.(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i \widehat{H}_{0}\left(t^{(k)}-t_{0}\right) / \hbar} \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(k)}-t_{0}\right) / \hbar}\right]\right) .
\end{align*}
$$

When the operators $\widehat{H}_{0}$ and $\widehat{V}$ commute, it is easily worked out that Eq. (31) is exactly the same as Eq. (2). However, if the operators $\widehat{H}_{0}$ and $\widehat{V}$ don't commute, it isn't guaranteed that the Eq. (31) putative formal perturbation series representation of $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$ converges.

Using the Eq. (3k) perturbation approximation of $n$th order in $\widehat{V}$ to $\exp \left(-i \widehat{H}\left(t-t_{0}\right) / \hbar\right)$, we now wish to reduce to quadrature the corresponding perturbation approximation to the time-dependent transition amplitude described by Eq. (1). Since Eq. (1) specifies that $\left(\psi_{l}^{(0)}, \psi_{i}^{(0)}\right)=0$, and since $\widehat{H}_{0} \psi_{j}^{(0)}=E_{j}^{(0)} \psi_{j}^{(0)}$, we obtain by application of Eq. (3k) to the Eq. (1) transition amplitude that,

$$
\begin{gather*}
\left(\psi_{l}^{(0)}, e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar} \psi_{i}^{(0)}\right)= \\
e^{-i E_{l}^{(0)}\left(t-t_{0}\right) / \hbar}\left((-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i E_{l}^{(0)}\left(t^{(1)}-t_{0}\right) / \hbar}\left(\psi_{l}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right) e^{-i E_{i}^{(0)}\left(t^{(1)}-t_{0}\right) / \hbar}+\right. \\
\sum_{k=2}^{n}\left[( - i / \hbar ) \int _ { t _ { 0 } } ^ { t } d t ^ { ( 1 ) } e ^ { + i E _ { l } ^ { ( 0 ) } ( t ^ { ( 1 ) } - t _ { 0 } ) / \hbar } \left(\psi_{l}^{(0)}, \widehat{V} e^{-i \widehat{H}_{0}\left(t^{(1)}-t_{0}\right) / \hbar} \ldots\right.\right.  \tag{4a}\\
\left.\left.\left.(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i \widehat{H}_{0}\left(t^{(k)}-t_{0}\right) / \hbar} \widehat{V} \psi_{i}^{(0)}\right) e^{-i E_{i}^{(0)}\left(t^{(k)}-t_{0}\right) / \hbar}\right]+O\left(\widehat{V}^{n+1}\right)\right) .
\end{gather*}
$$

To reduce each term on the right side of Eq. (4a) to quadrature, every occurrence of the $\widehat{V}$ operator in that term is expanded in the $\psi_{j}^{(0)}$ basis, i.e.,

$$
\begin{equation*}
\left(\phi_{1}, \widehat{V} \phi_{2}\right)=\sum_{j_{(1)} j_{(2)}}\left(\phi_{1}, \psi_{j_{(1)}}^{(0)}\right)\left(\psi_{j_{(1)}}^{(0)}, V \psi_{j_{(2)}}^{(0)}\right)\left(\psi_{j_{(2)}}^{(0)}, \phi_{2}\right), \tag{4b}
\end{equation*}
$$

after which the following two transparently true relations are applied,

$$
\begin{equation*}
e^{ \pm i \widehat{H}_{0}\left(t-t_{0}\right) / \hbar} \psi_{j}^{(0)}=e^{ \pm i E_{j}^{(0)}\left(t-t_{0}\right) / \hbar} \psi_{j}^{(0)} \quad \text { and } \quad\left(\psi_{j}^{(0)}, \psi_{j^{\prime}}^{(0)}\right)=\delta_{j j^{\prime}} \tag{4c}
\end{equation*}
$$

Upon completion of the $\psi_{j}^{(0)}$-basis expansion procedure described by Eqs. (4b) and (4c), Eq. (4a) reads,

$$
\begin{gather*}
\left(\psi_{l}^{(0)}, e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar} \psi_{i}^{(0)}\right)= \\
e^{-i E_{l}^{(0)}\left(t-t_{0}\right) / \hbar}\left((-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i E_{l}^{(0)}\left(t^{(1)}-t_{0}\right) / \hbar}\left(\psi_{l}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right) e^{-i E_{i}^{(0)}\left(t^{(1)}-t_{0}\right) / \hbar}+\right. \\
\sum_{k=2}^{n} \sum_{j_{(1)} \cdots j_{(k-1)}}\left[(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i E_{l}^{(0)}\left(t^{(1)}-t_{0}\right) / \hbar}\left(\psi_{l}^{(0)}, \widehat{V} \psi_{j_{(1)}}^{(0)}\right) e^{-i E_{j_{(1)}}^{(0)}\left(t^{(1)}-t_{0}\right) / \hbar} \ldots\right.  \tag{4d}\\
\left.\left.(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i E_{j_{(k-1)}}^{(0)}\left(t^{(k)}-t_{0}\right) / \hbar}\left(\psi_{j_{(k-1)}^{(0)}}^{(0)} \widehat{V} \psi_{i}^{(0)}\right) e^{-i E_{i}^{(0)}\left(t^{(k)}-t_{0}\right) / \hbar}\right]+O\left(\widehat{V}^{n+1}\right)\right),
\end{gather*}
$$

whose terms it is very useful to separate into time-dependent and time-independent factors as follows,

$$
\begin{gather*}
\left(\psi_{l}^{(0)}, e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar} \psi_{i}^{(0)}\right)= \\
e^{-i E_{l}^{(0)}\left(t-t_{0}\right) / \hbar}\left(\left[(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i\left(E_{l}^{(0)}-E_{i}^{(0)}\right)\left(t^{(1)}-t_{0}\right) / \hbar}\right]\left[\left(\psi_{l}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right)\right]+\right. \\
\sum_{k=2}^{n} \sum_{j_{(1)} \cdots j_{(k-1)}}\left[(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i\left(E_{l}^{(0)}-E_{j_{(1)}}^{(0)}\right)\left(t^{(1)}-t_{0}\right) / \hbar} \cdots\right.  \tag{4e}\\
\left.\left.(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i\left(E_{j_{(k-1)}}^{(0)}-E_{i}^{(0)}\right)\left(t^{(k)}-t_{0}\right) / \hbar}\right]\left[\left(\psi_{l}^{(0)}, \widehat{V} \psi_{j_{(1)}}^{(0)}\right) \cdots\left(\psi_{j_{(k-1)}}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right)\right]+O\left(\widehat{V}^{n+1}\right)\right) .
\end{gather*}
$$

The nested-integral time-dependent factors which occur in Eq. (4e) are of the general form,

$$
\begin{equation*}
(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i\left(\Delta E_{k}\right)\left(t^{(1)}-t_{0}\right) / \hbar} \cdots(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i\left(\Delta E_{1}\right)\left(t^{(k)}-t_{0}\right) / \hbar} \tag{5}
\end{equation*}
$$

Here we are interested in the long-time $t \rightarrow+\infty$ behavior of the Eq. (1) transition amplitudes, to which Eq. (4e) gives the perturbation approximations. We specifically wish to calculate perturbation approximations to long-time averaged transition rates (asymptotic transition rates), which are,

$$
\begin{equation*}
\lim _{t \rightarrow+\infty}\left\{\left|\left(\psi_{l}^{(0)}, e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar} \psi_{i}^{(0)}\right)\right|^{2} /\left(t-t_{0}\right)\right\} . \tag{6}
\end{equation*}
$$

Therefore we wish to obtain the $t \rightarrow+\infty$ limiting behavior of the Eq. (5) time-dependent entities. We begin with the simplest $k=1$ instance of Eq. (5),

$$
\begin{gather*}
\lim _{t \rightarrow+\infty}\left\{(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i\left(\Delta E_{1}\right)\left(t^{(1)}-t_{0}\right) / \hbar}\right\}=\lim _{t \rightarrow+\infty}\left\{\left(1-e^{+i\left(\Delta E_{1}\right)\left(t-t_{0}\right) / \hbar}\right) /(\Delta E)\right\}= \\
\lim _{t \rightarrow+\infty}\left\{\left(\left(1-\cos \left(\left(\Delta E_{1}\right)\left(t-t_{0}\right) / \hbar\right)\right) /\left(\Delta E_{1}\right)\right)-i\left(\sin \left(\left(\Delta E_{1}\right)\left(t-t_{0}\right) / \hbar\right) /\left(\Delta E_{1}\right)\right)\right\}=  \tag{7a}\\
P\left(1 /\left(\Delta E_{1}\right)\right)-i \pi \delta\left(\Delta E_{1}\right)
\end{gather*}
$$

where $P\left(1 /\left(\Delta E_{1}\right)\right)$ in Eq. (7a) stands for the principal value of $\left(1 /\left(\Delta E_{1}\right)\right)$. An alternative approach to obtaining this limiting behavior, which proves to be of decisive importance for dealing with arbitrary values of $k$ in Eq. (5) is,

$$
\begin{gather*}
\lim _{t \rightarrow+\infty}\left\{(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i\left(\Delta E_{1}\right)\left(t^{(1)}-t_{0}\right) / \hbar}\right\}=\lim _{\epsilon \rightarrow 0+}\left\{(-i / \hbar) \int_{t_{0}}^{+\infty} d t^{(1)} e^{+i\left(\Delta E_{1}+i \epsilon\right)\left(t^{(1)}-t_{0}\right) / \hbar}\right\}= \\
\lim _{\epsilon \rightarrow 0+}\left\{\left(\Delta E_{1}+i \epsilon\right)^{-1}\right\}=\lim _{\epsilon \rightarrow 0+}\left\{\left(\left(\Delta E_{1}\right) /\left(\left(\Delta E_{1}\right)^{2}+\epsilon^{2}\right)\right)-i\left(\epsilon /\left(\left(\Delta E_{1}\right)^{2}+\epsilon^{2}\right)\right)\right\}=  \tag{7b}\\
P\left(1 /\left(\Delta E_{1}\right)\right)-i \pi \delta\left(\Delta E_{1}\right) .
\end{gather*}
$$

Eqs. (7b) and (7a) show, inter alia, that the limit entities,

$$
\begin{equation*}
\lim _{\epsilon \rightarrow 0+}\left\{(-i / \hbar) \int_{t_{0}}^{+\infty} d t^{(1)} e^{+i(\Delta E+i \epsilon)\left(t^{(1)}-t_{0}\right) / \hbar}\right\}=\lim _{\epsilon \rightarrow 0+}\left\{((\Delta E)+i \epsilon)^{-1}\right\} \tag{7c}
\end{equation*}
$$

and,

$$
\begin{equation*}
\lim _{t \rightarrow+\infty}\left\{(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i(\Delta E)\left(t^{(1)}-t_{0}\right) / \hbar}\right\}=\lim _{t \rightarrow+\infty}\left\{\left(1-e^{+i(\Delta E)\left(t-t_{0}\right) / \hbar}\right) /(\Delta E)\right\}, \tag{7d}
\end{equation*}
$$

are interchangeable, a fact that will be very useful further on.
We now apply the approach used in Eq. (7b) to the evaluation of the $t \rightarrow+\infty$ behavior of the general Eq. (5) time-dependent entity,

$$
\begin{align*}
& \lim _{t \rightarrow+\infty}\left\{(-i / \hbar) \int_{t_{0}}^{t} d t^{(1)} e^{+i\left(\Delta E_{k}\right)\left(t^{(1)}-t_{0}\right) / \hbar} \cdots(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i\left(\Delta E_{1}\right)\left(t^{(k)}-t_{0}\right) / \hbar}\right\}= \\
& \lim _{\epsilon \rightarrow 0+}\left\{(-i / \hbar) \int_{t_{0}}^{+\infty} d t^{(1)} e^{+i\left(\Delta E_{k}+i \epsilon\right)\left(t^{(1)}-t_{0}\right) / \hbar} \cdots(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i\left(\Delta E_{1}\right)\left(t^{(k)}-t_{0}\right) / \hbar}\right\} \tag{7e}
\end{align*}
$$

which motivates us to attempt to evaluate all of the nested integrals which are defined as,

$$
\begin{gather*}
\mathcal{I}_{k}^{\epsilon}\left(\Delta E_{k}, \Delta E_{k-1}, \ldots, \Delta E_{1}\right) \stackrel{\text { def }}{=}(-i / \hbar) \int_{t_{0}}^{+\infty} d t^{(1)} e^{+i\left(\Delta E_{k}+i \epsilon\right)\left(t^{(1)}-t_{0}\right) / \hbar} \times \\
(-i / \hbar) \int_{t_{0}}^{t^{(1)}} d t^{(2)} e^{+i\left(\Delta E_{k-1}\right)\left(t^{(2)}-t_{0}\right) / \hbar} \cdots(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i\left(\Delta E_{1}\right)\left(t^{(k)}-t_{0}\right) / \hbar} \tag{7f}
\end{gather*}
$$

From Eq. (7b) we of course already know that $\mathcal{I}_{1}^{\epsilon}\left(\Delta E_{1}\right)=\left(\Delta E_{1}+i \epsilon\right)^{-1}$. By carrying out an integration by parts on $\mathcal{I}_{k+1}^{\epsilon}\left(\Delta E_{k+1}, \Delta E_{k}, \ldots, \Delta E_{1}\right)$, we obtain a recurrence relation which, along with the value of $\mathcal{I}_{1}^{\epsilon}\left(\Delta E_{1}\right)$, leads to a closed-form result for $\mathcal{I}_{k}^{\epsilon}\left(\Delta E_{k}, \Delta E_{k-1}, \ldots, \Delta E_{1}\right)$. The terms of the integration by parts that are evaluated at the endpoints $t^{(1)}=t_{0}$ and $t^{(1)} \rightarrow+\infty$ turn out to both vanish,

$$
\begin{gather*}
\mathcal{I}_{k+1}^{\epsilon}\left(\Delta E_{k+1}, \Delta E_{k}, \ldots, \Delta E_{1}\right)= \\
(-i / \hbar) \int_{t_{0}}^{+\infty} d t^{(1)} e^{+i\left(\Delta E_{k+1}+i \epsilon\right)\left(t^{(1)}-t_{0}\right) / \hbar}(-i / \hbar) \int_{t_{0}}^{t^{(1)}} d t^{(2)} e^{+i\left(\Delta E_{k}\right)\left(t^{(2)}-t_{0}\right) / \hbar} \times \\
(-i / \hbar) \int_{t_{0}}^{t^{(2)}} d t^{(3)} e^{+i\left(\Delta E_{k-1}\right)\left(t^{(3)}-t_{0}\right) / \hbar} \cdots(-i / \hbar) \int_{t_{0}}^{t^{(k)}} d t^{(k+1)} e^{+i\left(\Delta E_{1}\right)\left(t^{(k+1)}-t_{0}\right) / \hbar}=  \tag{7~g}\\
\left(\Delta E_{k+1}+i \epsilon\right)^{-1}(-i / \hbar) \int_{t_{0}}^{+\infty} d t^{(1)} e^{+i\left(\Delta E_{k+1}+\Delta E_{k}+i \epsilon\right)\left(t^{(1)}-t_{0}\right) / \hbar} \times \\
(-i / \hbar) \int_{t_{0}}^{t^{(1)}} d t^{(2)} e^{+i\left(\Delta E_{k-1}\right)\left(t^{(2)}-t_{0}\right) / \hbar} \cdots(-i / \hbar) \int_{t_{0}}^{t^{(k-1)}} d t^{(k)} e^{+i\left(\Delta E_{1}\right)\left(t^{(k)}-t_{0}\right) / \hbar}= \\
\left(\Delta E_{k+1}+i \epsilon\right)^{-1} \mathcal{I}_{k}^{\epsilon}\left(\Delta E_{k+1}+\Delta E_{k}, \Delta E_{k-1}, \ldots, \Delta E_{1}\right) .
\end{gather*}
$$

The relation $\mathcal{I}_{k+1}^{\epsilon}\left(\Delta E_{k+1}, \Delta E_{k}, \ldots, \Delta E_{1}\right)=\left(\Delta E_{k+1}+i \epsilon\right)^{-1} \mathcal{I}_{k}^{\epsilon}\left(\Delta E_{k+1}+\Delta E_{k}, \Delta E_{k-1}, \ldots, \Delta E_{1}\right)$ of recurrence obtained in Eq. ( 7 g ) yields, starting from $\mathcal{I}_{1}^{\epsilon}\left(\Delta E_{1}\right)=\left(\Delta E_{1}+i \epsilon\right)^{-1}$, that,

$$
\begin{gather*}
\mathcal{I}_{2}^{\epsilon}\left(\Delta E_{2}, \Delta E_{1}\right)=\left(\Delta E_{2}+i \epsilon\right)^{-1} \mathcal{I}_{1}^{\epsilon}\left(\Delta E_{2}+\Delta E_{1}\right)= \\
\left(\Delta E_{2}+i \epsilon\right)^{-1}\left(\Delta E_{2}+\Delta E_{1}+i \epsilon\right)^{-1} \\
\mathcal{I}_{3}^{\epsilon}\left(\Delta E_{3}, \Delta E_{2}, \Delta E_{1}\right)=\left(\Delta E_{3}+i \epsilon\right)^{-1} \mathcal{I}_{2}^{\epsilon}\left(\Delta E_{3}+\Delta E_{2}, \Delta E_{1}\right)= \\
\left(\Delta E_{3}+i \epsilon\right)^{-1}\left(\Delta E_{3}+\Delta E_{2}+i \epsilon\right)^{-1}\left(\Delta E_{3}+\Delta E_{2}+\Delta E_{1}+i \epsilon\right)^{-1}, \\
\mathcal{I}_{4}^{\epsilon}\left(\Delta E_{4}, \Delta E_{3}, \Delta E_{2}, \Delta E_{1}\right)=\left(\Delta E_{4}+i \epsilon\right)^{-1} \mathcal{I}_{3}^{\epsilon}\left(\Delta E_{4}+\Delta E_{3}, \Delta E_{2}, \Delta E_{1}\right)=  \tag{7h}\\
\left(\Delta E_{4}+i \epsilon\right)^{-1}\left(\Delta E_{4}+\Delta E_{3}+i \epsilon\right)^{-1}\left(\Delta E_{4}+\Delta E_{3}+\Delta E_{2}+i \epsilon\right)^{-1}\left(\Delta E_{4}+\Delta E_{3}+\Delta E_{2}+\Delta E_{1}+i \epsilon\right)^{-1}, \\
\text { so obviously, } \mathcal{I}_{k}^{\epsilon}\left(\Delta E_{k}, \Delta E_{k-1}, \ldots, \Delta E_{1}\right)=\left(\Delta E_{k}+i \epsilon\right)^{-1}\left(\Delta E_{k}+\Delta E_{k-1}+i \epsilon\right)^{-1} \cdots \times \\
\left(\Delta E_{k}+\Delta E_{k-1}+\cdots+\Delta E_{2}+i \epsilon\right)^{-1}\left(\Delta E_{k}+\Delta E_{k-1}+\cdots+\Delta E_{1}+i \epsilon\right)^{-1},
\end{gather*}
$$

where the final (general) result given in Eq. (7h) can easily be proved by induction using the Eq. (7g) recurrence relation. The nested-integral time-dependent factors which occur in the Eq. (4e) perturbation approximations to Eq. (1) correspond to the Eq. (5) nested-integral form via the following relations,

$$
\begin{gather*}
\left(\Delta E_{k}\right)=\left(E_{l}^{(0)}-E_{j_{(1)}}^{(0)}\right),\left(\Delta E_{k-1}\right)=\left(E_{j_{(1)}}^{(0)}-E_{j_{(2)}}^{(0)}\right), \cdots \\
\left(\Delta E_{2}\right)=\left(E_{j_{(k-2)}}^{(0)}-E_{j_{(k-1)}}^{(0)}\right) \text { and }\left(\Delta E_{1}\right)=\left(E_{j_{(k-1)}}^{(0)}-E_{i}^{(0)}\right), \tag{7i}
\end{gather*}
$$

which implies that,

$$
\begin{gather*}
\left(\Delta E_{k}\right)=\left(E_{l}^{(0)}-E_{j_{(1)}}^{(0)}\right),\left(\Delta E_{k}+\Delta E_{k-1}\right)=\left(E_{l}^{(0)}-E_{j_{(2)}}^{(0)}\right), \cdots,  \tag{7j}\\
\left(\Delta E_{k}+\Delta E_{k-1}+\cdots+\Delta E_{2}\right)=\left(E_{l}^{(0)}-E_{j_{(k-1)}}^{(0)}\right) \text { and }\left(\Delta E_{k}+\Delta E_{k-1}+\cdots+\Delta E_{1}\right)=\left(E_{l}^{(0)}-E_{i}^{(0)}\right)
\end{gather*}
$$

Inserting the results given by Eqs. (7h) and (7j) into Eq. (4e) yields,

$$
\begin{gather*}
\lim _{t \rightarrow+\infty}\left\{e^{+i E_{l}^{(0)}\left(t-t_{0}\right) / \hbar}\left(\psi_{l}^{(0)}, e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar} \psi_{i}^{(0)}\right)\right\}=\lim _{\epsilon \rightarrow 0+}\left\{\left(\left(E_{l}^{(0)}-E_{i}^{(0)}\right)+i \epsilon\right)^{-1} \times\right. \\
{\left[\left(\psi_{l}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right)+\sum_{k=2}^{n} \sum_{j_{(1)} \cdots j_{(k-1)}}\left(\left(\left(\psi_{l}^{(0)}, \widehat{V} \psi_{j_{(1)}}^{(0)}\right)\left(\left(E_{l}^{(0)}-E_{j_{(1)}}^{(0)}\right)+i \epsilon\right)\right)^{-1} \cdots\right.\right.}  \tag{7k}\\
\left.\left.\left.\left(\left(E_{l}^{(0)}-E_{j_{(k-1)}}^{(0)}\right)+i \epsilon\right)\right)^{-1}\left(\left(\psi_{j_{(k-1)}}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right)\right)+O\left(\widehat{V}^{n+1}\right)\right]\right\}
\end{gather*}
$$

The Eq. (7k) result also formally yields what we are specifically interested in, namely the perturbation approximations to the Eq. (6) long-time averaged transition rate (the asymptotic transition rate), as,

$$
\begin{gather*}
\lim _{t \rightarrow+\infty}\left\{\left|\left(\psi_{l}^{(0)}, e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar} \psi_{i}^{(0)}\right)\right|^{2} /\left(t-t_{0}\right)\right\}= \\
\lim _{t \rightarrow+\infty} \lim _{\epsilon \rightarrow 0+}\left\{\left(\left(\left(E_{l}^{(0)}-E_{i}^{(0)}\right)^{2}+\epsilon^{2}\right)\left(t-t_{0}\right)\right)^{-1} \times\right. \\
\mid\left(\psi_{l}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right)+\sum_{k=2}^{n} \sum_{j_{(1)} \cdots j_{(k-1)}}\left(\left(\left(\psi_{l}^{(0)}, \widehat{V} \psi_{j_{(1)}}^{(0)}\right)\left(\left(E_{l}^{(0)}-E_{j_{(1)}}^{(0)}\right)+i \epsilon\right)\right)^{-1} \cdots\right.  \tag{7l}\\
\left.\left.\left(\left(E_{l}^{(0)}-E_{j_{(k-1)}}^{(0)}\right)+i \epsilon\right)\right)^{-1}\left(\left(\psi_{j_{(k-1)}}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right)\right)+\left.O\left(\widehat{V}^{n+1}\right)\right|^{2}\right\},
\end{gather*}
$$

but the Eq. (7l) mixed limit entity,

$$
\begin{equation*}
\lim _{t \rightarrow+\infty} \lim _{\epsilon \rightarrow 0+}\left\{\left(\left(\left(E_{l}^{(0)}-E_{i}^{(0)}\right)^{2}+\epsilon^{2}\right)\left(t-t_{0}\right)\right)^{-1}\right\} \tag{7~m}
\end{equation*}
$$

seems ill-defined at first glance. Eqs. (7c) and (7d), however, tell us that $\lim _{\epsilon \rightarrow 0+}\left\{(\Delta E+i \epsilon)^{-1}\right\}$ is interchangeable with $\lim _{t \rightarrow+\infty}\left\{\left(1-\exp \left(+i(\Delta E)\left(t-t_{0}\right) / \hbar\right)\right) /(\Delta E)\right\}$, which resolves the mixed limit puzzle,

$$
\begin{gather*}
\lim _{t \rightarrow+\infty} \lim _{\epsilon \rightarrow 0+}\left\{\left(\left(\left(E_{l}^{(0)}-E_{i}^{(0)}\right)^{2}+\epsilon^{2}\right)\left(t-t_{0}\right)\right)^{-1}\right\}= \\
\lim _{t \rightarrow+\infty}\left\{\mid 1-e^{\left.+i\left(E_{l}^{(0)}-E_{i}^{(0)}\right)\left(t-t_{0}\right) /\left.\hbar\right|^{2} /\left(\left(E_{l}^{(0)}-E_{i}^{(0)}\right)^{2}\left(t-t_{0}\right)\right)\right\}=}\right.  \tag{7n}\\
\lim _{t \rightarrow+\infty}\left\{2\left(1-\cos \left(\left(E_{l}^{(0)}-E_{i}^{(0)}\right)\left(t-t_{0}\right) / \hbar\right)\right) /\left(\left(E_{l}^{(0)}-E_{i}^{(0)}\right)^{2}\left(t-t_{0}\right)\right)\right\}=(2 \pi / \hbar) \delta\left(E_{l}^{(0)}-E_{i}^{(0)}\right),
\end{gather*}
$$

so more transparently, the perturbation approximations to the Eq. (6) asymptotic transition rate are,

$$
\begin{gather*}
\lim _{t \rightarrow+\infty}\left\{\left|\left(\psi_{l}^{(0)}, e^{-i \widehat{H}\left(t-t_{0}\right) / \hbar} \psi_{i}^{(0)}\right)\right|^{2} /\left(t-t_{0}\right)\right\}=(2 \pi / \hbar) \delta\left(E_{l}^{(0)}-E_{i}^{(0)}\right) \times \\
\lim _{\epsilon \rightarrow 0+}\left\{\mid\left(\psi_{l}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right)+\sum_{k=2}^{n} \sum_{j_{(1)} \cdots j_{(k-1)}}\left(\left(\left(\psi_{l}^{(0)}, \widehat{V} \psi_{j_{(1)}}^{(0)}\right)\left(\left(E_{l}^{(0)}-E_{j_{(1)}}^{(0)}\right)+i \epsilon\right)\right)^{-1} \cdots\right.\right.  \tag{7o}\\
\left.\left.\left(\left(E_{l}^{(0)}-E_{j_{(k-1)}}^{(0)}\right)+i \epsilon\right)\right)^{-1}\left(\left(\psi_{j_{(k-1)}}^{(0)}, \widehat{V} \psi_{i}^{(0)}\right)\right)+\left.O\left(\widehat{V}^{n+1}\right)\right|^{2}\right\}
\end{gather*}
$$

## Perturbation approximations in nonrelativistic-particle potential scattering

The total cross section $\sigma$ for a free-particle collision interaction is an asymptotic transition rate of the type approximated to $n$th order in the perturbation $\widehat{V}$ by Eq. (7o), divided by the initial free-particle flux and summed over all final states $\psi_{l}^{(0)}$. A variety of partial cross sections are defined by omitting selected parts of the sum over the final states $\psi_{l}^{(0)}$. In this section we use the nth-order perturbation approximation to the asymptotic transition rate that is given by Eq. (70) to obtain the corresponding perturbation approximation to the cross section for the scattering of a nonrelativistic free particle-whose "unperturbed" Hamilton operator is $\widehat{H}_{0}=|\widehat{\mathbf{p}}|^{2} /(2 m)$-by a localized static potential-energy operator $V(\widehat{\mathbf{r}})$. Since Eq. (7o) implicitly deals with "unperturbed" states $\psi_{j}^{(0)}$ which are normalized to unity, we definitely cannot use the familiar continuum plane-wave momentum eigenstates of a free nonrelativistic particle whose Hamiltonian operator is $\widehat{H}_{0}=|\widehat{\mathbf{p}}|^{2} /(2 m)$. We therefore replace the continuum plane-wave momentum eigenstates by momentum eigenstates which adhere to periodic boundary conditions in a cubical box of finite, but arbitrarily large, volume $\mathcal{V}$. The detailed form of the discrete cubical-box-periodic normalized-to-unity momentum eigenstates is,

$$
\begin{equation*}
\psi_{\left(n_{x}, n_{y}, n_{z}\right)}(\mathbf{r})=\mathcal{V}^{-\frac{1}{2}} \exp \left(2 \pi i\left(x n_{x}+y n_{y}+z n_{z}\right) / \mathcal{V}^{\frac{1}{3}}\right)=\mathcal{V}^{-\frac{1}{2}} e^{i \mathbf{p} \cdot \mathbf{r} / \hbar} \tag{8a}
\end{equation*}
$$

where $n_{x}, n_{y}$ and $n_{z}$ are integers. Eq. (8a) yields that the momentum eigenvalue $\mathbf{p}$ of $\psi_{\left(n_{x}, n_{y}, n_{z}\right)}(\mathbf{r})$ is,

$$
\begin{equation*}
\mathbf{p}=\left(2 \pi \hbar / \mathcal{V}^{\frac{1}{3}}\right)\left(n_{x}, n_{y}, n_{z}\right) \tag{8b}
\end{equation*}
$$

which shows that these discrete momentum eigenvalues tend toward a continuum as the box volume $\mathcal{V} \rightarrow \infty$.
Eq. (7o) features sums over the quantum numbers $j$ of the "unperturbed" states $\psi_{j}^{(0)}$, and of course such a sum (over all final states) is fundamental to the definition of the total cross section $\sigma$. In the nonrelativistic potential scattering case, we see from Eq. (8a) that those sums over $j$ are sums over all of the integer triplets $\left(n_{x}, n_{y}, n_{z}\right)$, and since the "unperturbed" free particle's momentum $\mathbf{p}=\left(p_{x}, p_{y}, p_{z}\right)=$ $\left(2 \pi \hbar / \mathcal{V}^{\frac{1}{3}}\right)\left(n_{x}, n_{y}, n_{z}\right)$, of course $\left(n_{x}, n_{y}, n_{z}\right)=\left(\mathcal{V}^{\frac{1}{3}} /(2 \pi \hbar)\right)\left(p_{x}, p_{y}, p_{z}\right)$, and since the momentum eigenvalues $\left(p_{x}, p_{y}, p_{z}\right)$ approach a continuum as the box volume $\mathcal{V} \rightarrow \infty$, then for a sufficiently large box volume $\mathcal{V}$,

$$
\begin{gather*}
\sum_{\left(n_{x}, n_{y}, n_{z}\right)}=\sum_{n_{x}} \sum_{n_{y}} \sum_{n_{z}}=  \tag{8c}\\
\left(\mathcal{V}^{\frac{1}{3}} /(2 \pi \hbar)\right) \int d p_{x}\left(\mathcal{V}^{\frac{1}{3}} /(2 \pi \hbar)\right) \int d p_{y}\left(\mathcal{V}^{\frac{1}{3}} /(2 \pi \hbar)\right) \int d p_{z}=\left(\mathcal{V} /(2 \pi \hbar)^{3}\right) \int d^{3} \mathbf{p}
\end{gather*}
$$

Thus, in the nonrelativistic potential scattering case, $\sum_{j}$ in Eq. (70) becomes,

$$
\begin{equation*}
\sum_{j} \longrightarrow\left(\mathcal{V} /(2 \pi \hbar)^{3}\right) \int d^{3} \mathbf{p}_{j} \tag{8d}
\end{equation*}
$$

Furthermore, since Eq. (8a) tells us that in the nonrelativistic potential scattering case the $\psi_{j}^{(0)}$ of Eq. (7o) is $\mathcal{V}^{-\frac{1}{2}} \exp \left(i \mathbf{p}_{j} \cdot \mathbf{r} / \hbar\right)$, and also, since in that case the $\widehat{V}$ of Eq. (70) is the static potential energy operator $V(\widehat{\mathbf{r}})$, we see that in the nonrelativistic potential scattering case the entities $\left(\psi_{m}^{(0)}, \widehat{V} \psi_{j}^{(0)}\right.$ ) of Eq. (7o) become,

$$
\begin{equation*}
\left(\psi_{m}^{(0)}, \widehat{V} \psi_{j}^{(0)}\right) \longrightarrow \mathcal{V}^{-1} V_{\mathcal{F}}\left(\mathbf{p}_{m}-\mathbf{p}_{j}\right), \text { where } V_{\mathcal{F}}(\mathbf{q}) \stackrel{\text { def }}{=} \int d^{3} \mathbf{r} \exp (-i \mathbf{q} \cdot \mathbf{r} / \hbar) V(\mathbf{r}) . \tag{8e}
\end{equation*}
$$

Also the $E_{j}^{(0)}$ of Eq. (7o) is of course $\left|\mathbf{p}_{j}\right|^{2} /(2 m)$ in the nonrelativistic potential scattering case,

$$
\begin{equation*}
E_{j}^{(0)} \longrightarrow\left|\mathbf{p}_{j}\right|^{2} /(2 m) \tag{8f}
\end{equation*}
$$

Finally, the flux of the initial nonrelativistic free particle of momentum $\mathbf{p}_{i}$ is its speed $\left(\left|\mathbf{p}_{i}\right| / m\right)$ divided by its wave-function normalization volume $\mathcal{V}$. Dividing Eq. (7o) by that flux, specializing the rest of Eq. (7o) to nonrelativistic potential scattering by applying Eqs. (8d)-(8f) to it, and summing the result over all of the final states $\psi_{l}^{(0)}$ yields the perturbation approximation of $n$th order in the localized static potential operator $V(\widehat{\mathbf{r}})$ to the total cross section $\sigma$ for the scattering of a nonrelativistic free particle by that potential,

$$
\begin{gather*}
\sigma=\left(m /\left|\mathbf{p}_{i}\right|\right)(2 \pi \hbar)^{-3} \int d^{3} \mathbf{p}_{l}(2 \pi / \hbar)(2 m) \delta\left(\left|\mathbf{p}_{l}\right|^{2}-\left|\mathbf{p}_{i}\right|^{2}\right) \mid V_{\mathcal{F}}\left(\mathbf{p}_{l}-\mathbf{p}_{i}\right)+ \\
\lim _{\epsilon \rightarrow 0+}\left\{\sum_{k=2}^{n}(2 \pi \hbar)^{-3} \int d^{3} \mathbf{p}_{j_{(1)}} \cdots(2 \pi \hbar)^{-3} \int d^{3} \mathbf{p}_{j_{(k-1)}} V_{\mathcal{F}}\left(\mathbf{p}_{l}-\mathbf{p}_{j_{(1)}}\right)(2 m)\left(\left|\mathbf{p}_{l}\right|^{2}-\left|\mathbf{p}_{j_{(1)}}\right|^{2}+i \epsilon\right)^{-1} \cdots\right.  \tag{8~g}\\
\left.(2 m)\left(\left|\mathbf{p}_{l}\right|^{2}-\left|\mathbf{p}_{j_{(k-1)}}\right|^{2}+i \epsilon\right)^{-1} V_{\mathcal{F}}\left(\mathbf{p}_{j_{(k-1)}}-\mathbf{p}_{i}\right)\right\}+\left.O\left((V(\widehat{\mathbf{r}}))^{n+1}\right)\right|^{2}
\end{gather*}
$$

The box volume $\mathcal{V}$ has canceled out in the Eq. ( 8 g ) perturbation approximations to the total cross section $\sigma$ for nonrelativistic potential scattering, as physical reasoning very strongly indeed suggests that it must in the limit of $\mathcal{V} \rightarrow \infty$. The "unperturbed-energy" conserving delta-function factor $(2 m) \delta\left(\left|\mathbf{p}_{l}\right|^{2}-\left|\mathbf{p}_{i}\right|^{2}\right)$ that is present in Eq. (8g) makes it possible to immediately evaluate the $\int_{0}^{\infty}\left|\mathbf{p}_{l}\right|^{2} d\left|\mathbf{p}_{l}\right| \cdots$ part of the $\int d^{3} \mathbf{p}_{l} \cdots$ integral that occurs in the Eq. ( 8 g ) expression. The integration over the differential solid angle $d \Omega_{\mathbf{p}_{l}}$ of the final particle momentum $\mathbf{p}_{l}$ remains to be carried out, but if we choose to simply omit that differential solid-angle integration, we will have obtained the perturbation approximations to the very useful differential cross section $d \sigma / d \Omega_{\mathbf{p}_{l}}$ for nonrelativistic potential scattering; it is easily worked out from Eq. (8g) to be,

$$
\begin{gather*}
d \sigma / d \Omega_{\mathbf{p}_{l}}=\mid\left(m /\left(2 \pi \hbar^{2}\right)\right)\left(V_{\mathcal{F}}\left(\mathbf{p}_{l}-\mathbf{p}_{i}\right)+\lim _{\epsilon \rightarrow 0+}\left\{\sum_{k=2}^{n}(2 \pi \hbar)^{-3} \int d^{3} \mathbf{p}_{j_{(1)}} \cdots(2 \pi \hbar)^{-3} \int d^{3} \mathbf{p}_{j_{(k-1)}} \times\right.\right. \\
V_{\mathcal{F}}\left(\mathbf{p}_{l}-\mathbf{p}_{j_{(1)}}\right)(2 m)\left(\left|\mathbf{p}_{i}\right|^{2}-\left|\mathbf{p}_{j_{(1)}}\right|^{2}+i \epsilon\right)^{-1} \cdots(2 m)\left(\left|\mathbf{p}_{i}\right|^{2}-\left|\mathbf{p}_{j_{(k-1)}}\right|^{2}+i \epsilon\right)^{-1} \times  \tag{8h}\\
\left.\left.\left.V_{\mathcal{F}}\left(\mathbf{p}_{j_{(k-1)}}-\mathbf{p}_{i}\right)\right\}\right)_{\left|\mathbf{p}_{l}\right|=\left|\mathbf{p}_{i}\right|}+O\left((V(\widehat{\mathbf{r}}))^{n+1}\right)\right)\left.\right|^{2} .
\end{gather*}
$$

A specific simple example of Eq. (8h) is the lowest-order perturbation approximation to the differential cross section for scattering from a Yukawa potential $V(\mathbf{r})=\varepsilon^{2} \exp \left(-|\mathbf{r}| / r_{0}\right) /|\mathbf{r}|$, where the coupling strength $\varepsilon^{2}$ has the dimension of energy times length. The lowest-order perturbation approximation to the "scattering length" for this Yukawa potential - the absolute square of which is the corresponding approximation to the differential cross section-is, from Eq. (8h),

$$
\begin{equation*}
\left(m /\left(2 \pi \hbar^{2}\right)\right) V_{\mathcal{F}}^{(\text {Yukawa) }}\left(\mathbf{p}_{l}-\mathbf{p}_{i}\right), \tag{9a}
\end{equation*}
$$

where,

$$
\begin{gather*}
V_{\mathcal{F}}^{(\text {Yukawa })}(\mathbf{q})=\varepsilon^{2} \int d^{3} \mathbf{r} \exp (-i \mathbf{q} \cdot \mathbf{r} / \hbar) \exp \left(-|\mathbf{r}| / r_{0}\right) /|\mathbf{r}|= \\
\varepsilon^{2} \int_{0}^{\infty} d r r e^{-r / r_{0}}(2 \pi) \int_{0}^{\pi} d \theta \sin \theta e^{-i|\mathbf{q}| r \cos \theta / \hbar}=\varepsilon^{2}(2 \pi) \int_{0}^{\infty} d r r e^{-r / r_{0}} \int_{-1}^{1} d \alpha e^{-i|\mathbf{q}| r \alpha / \hbar}=  \tag{9b}\\
\varepsilon^{2}(4 \pi \hbar /|\mathbf{q}|) \int_{0}^{\infty} d r e^{-r / r_{0}} \sin (|\mathbf{q}| r / \hbar)=\varepsilon^{2}(4 \pi \hbar /|\mathbf{q}|) \operatorname{Im}\left(\int_{0}^{\infty} d r e^{-r\left(\left(1 / r_{0}\right)-i(|\mathbf{q}| / \hbar)\right)}\right)= \\
\varepsilon^{2}(4 \pi)\left((|\mathbf{q}| / \hbar)^{2}+\left(1 / r_{0}\right)^{2}\right)^{-1}
\end{gather*}
$$

Therefore this Yukawa potential's lowest-order "scattering length" comes out to be,

$$
\begin{equation*}
\left(m /\left(2 \pi \hbar^{2}\right)\right) V_{\mathcal{F}}^{(\text {Yukawa })}\left(\mathbf{p}_{l}-\mathbf{p}_{i}\right)=\varepsilon^{2}(2 m)\left(\left|\mathbf{p}_{l}-\mathbf{p}_{i}\right|^{2}+\left(\hbar / r_{0}\right)^{2}\right)^{-1}, \text { where }\left|\mathbf{p}_{l}\right|=\left|\mathbf{p}_{i}\right| \tag{9c}
\end{equation*}
$$

This Yukawa potential becomes a nuclear Coulomb scattering potential when $r_{0} \rightarrow \infty$ and $\varepsilon^{2}=Z_{1} Z_{2} e^{2}$, in which case the lowest-order perturbation approximation to the "scattering length" is,

$$
\begin{equation*}
Z_{1} Z_{2} e^{2} m /\left(\left|\mathbf{p}_{i}\right|^{2}\left(1-\cos \theta_{(l i)}\right)\right) \tag{9c}
\end{equation*}
$$

and the corresponding approximation to the differential cross section is of course the square of Eq. (9c). Ernest Rutherford obtained exactly that differential cross section result classically by relating the final asymptote of the classical particle's hyperbolic trajectory to its initial impact parameter. Although we have only calculated this result quantum mechanically in the lowest-order perturbation approximation, it has been established that the higher-order corrections to this "scattering length" result are the perturbation expansion of a pure phase factor, which of course becomes exactly unity upon taking the absolute square of the "scattering length" to obtain the differential cross section. Thus nonrelativistic Coulomb potential scattering presents the unusual circumstance of perfect agreement of exact quantum mechanics with its lowest-order perturbation approximation, and also with the classical result.

