

Quantum Mechanics Notes

Duncan MacIntyre

November 3, 2023

Contents

1	Approximation methods	2
1(a)	Time-independent perturbation theory	2
1(a).1	The zero-order energies	2
1(a).2	The zero-order states	2
1(a).3	Rearranging the Schrödinger equation	3
1(a).4	First order energy	5
2	Identical particles	5
2(a)	Pauli exclusion principle	5
3	Time-dependent perturbation theory in the interaction picture	6

1 Approximation methods

1(a) Time-independent perturbation theory

Time-independent perturbation theory lets us study Hamiltonians of the form $H = H_0 + \lambda H'$ where H_0 is a Hamiltonian that we can solve exactly and H' is some change (a “perturbation”) that we’re interested in. λ is a constant scalar; we will come up with an approximation that is good for small enough values of λ .

Our goal is to approximate the eigenstates $|\psi\rangle$ and eigenvalues E of the eigenvalue problem

$$H|\psi\rangle = E|\psi\rangle.$$

One could imagine that there might be some states $|\psi^{(m)}\rangle$ and values $E^{(m)}$ so that we can write

$$|\psi\rangle = |\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \lambda^2 |\psi^{(2)}\rangle + \dots \quad (1)$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \quad (2)$$

for small enough λ . We will assume that some approximation of this type works and then try to determine what the $|\psi^{(m)}\rangle$ and $E^{(m)}$ must be.

Gap!!! There should be some justification of whether/why the series above converge and an explanation of the theory of asymptotic approximations that allows us to make these approximations even when the series diverge.

In our derivations, let us suppose that H_0 has eigenstates $|n\rangle$ and eigenvalues $E_n^{(0)}$ for $n = 1, 2, 3, \dots$, that is,

$$H_0 |n\rangle = E_n^{(0)} |n\rangle, \quad n = 1, 2, 3, \dots$$

Perturbation theory also works for continuous spectra but it will keep our notation simpler to talk about the discrete case.

1(a).1 The zero-order energies

As $\lambda \rightarrow 0$, we should have $E \rightarrow E_n^{(0)}$ for some n . Looking at (2), we must have $E^{(0)} = E_n^{(0)}$. This suggests that we give our state an index. From now on, let’s write $|\psi_n\rangle$ instead of $|\psi\rangle$, E_n instead of E , $|\psi_n^{(m)}\rangle$ instead of $|\psi^{(m)}\rangle$, and $E_n^{(m)}$ instead of $E^{(m)}$. We have

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \quad (3)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (4)$$

(For a degenerate spectrum, there could be multiple possible n —just choose one. It turns out that we are able to make this one-to-one map between eigenstates of H_0 and eigenstates of H but there are multiple possible maps because we could choose any of the states with energy E_n .)

1(a).2 The zero-order states

Now, we have $H_0 |\psi\rangle = E_n^{(0)} |\psi\rangle$, so $|\psi_n\rangle$ is an eigenstate of H_0 with eigenvalue $E_n^{(0)}$, so $|\psi_n\rangle$ is a superposition of the states that have energy $E_n^{(0)}$. Let D_n be the set of indices m such that $E_m^{(0)} = E_n^{(0)}$. Then we can write

$$|\psi_n\rangle = \sum_{m \in D_n} c_m |m\rangle$$

for some coefficients c_m . To find the c_m , we turn to the Schrödinger equation. We have

$$\begin{aligned} (H_0 + \lambda H') |\psi_n\rangle &= E_n |\psi_n\rangle \\ (H_0 + \lambda H') \left[|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \mathcal{O}(\lambda^2) \right] &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \mathcal{O}(\lambda^2) \right) \left[|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \mathcal{O}(\lambda^2) \right] \\ H_0 |\psi_n^{(0)}\rangle + \lambda \left(H' |\psi_n^{(0)}\rangle + H_0 |\psi_n^{(1)}\rangle \right) + \mathcal{O}(\lambda^2) &= E_n^{(0)} |\psi_n^{(0)}\rangle + \lambda \left(E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle \right) + \mathcal{O}(\lambda^2). \end{aligned}$$

In the zeroth order of λ this gives $H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$, confirming what we already know: $|\psi_n^{(0)}\rangle$ is an eigenstate of H_0 with eigenvalue $E_n^{(0)}$. In the first order of λ we get

$$H' |\psi_n^{(0)}\rangle + H_0 |\psi_n^{(1)}\rangle = E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle.$$

Multiplying with $\langle m|$, where $m \in D_n$,

$$\begin{aligned} \langle m| H' |\psi_n^{(0)}\rangle + \langle m| H_0 |\psi_n^{(1)}\rangle &= E_n^{(0)} \langle m| \psi_n^{(1)}\rangle + E_n^{(1)} \langle m| \psi_n^{(0)}\rangle \\ \langle m| H' |\psi_n^{(0)}\rangle + \cancel{E_n^{(0)} \langle m| \psi_n^{(1)}\rangle} &= \cancel{E_n^{(0)} \langle m| \psi_n^{(1)}\rangle} + E_n^{(1)} \langle m| \psi_n^{(0)}\rangle \\ \langle m| \psi_n^{(0)}\rangle &= \frac{\langle m| H' |\psi_n^{(0)}\rangle}{E_n^{(1)}}. \end{aligned}$$

Gap!!! This part needs to be added. It should include discussion of the orthonormality of the states.

1(a).3 Rearranging the Schrödinger equation

To get the first- and second-order corrections, we start by multiplying the Schrödinger equation by $\langle \psi_m^{(0)}|$. We get

$$\begin{aligned} \langle \psi_m^{(0)}| (H_0 + \lambda H') |\psi_n\rangle &= E_n \langle \psi_m^{(0)}| \psi_n\rangle \\ E_m^{(0)} \langle \psi_m^{(0)}| \psi_n\rangle + \langle \psi_m^{(0)}| \lambda H' |\psi_n\rangle &= E_n \langle \psi_m^{(0)}| \psi_n\rangle \\ \langle \psi_m^{(0)}| \psi_n\rangle &= \frac{\langle \psi_m^{(0)}| \lambda H' |\psi_n\rangle}{E_n - E_m^{(0)}} \\ \langle \psi_m^{(0)}| \psi_n\rangle &= \frac{\lambda \langle \psi_m^{(0)}| H' \left(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \mathcal{O}(\lambda^2) \right)}{E_n - E_m^{(0)}} \end{aligned} \tag{5}$$

Let's examine the denominator. We'll consider the two cases where n is/is not degenerate with m .

Let D_n be the set of indices m such that $E_m^{(0)} = E_n^{(0)}$. If $m \notin D_n$ then

$$\begin{aligned} E_n - E_m^{(0)} &= \left(E_n^{(0)} - E_m^{(0)} \right) + \lambda E_n^{(1)} + \lambda^2 E_n^{(1)} + \mathcal{O}(\lambda^3) \\ &= \left(E_n^{(0)} - E_m^{(0)} \right) [1 + \mathcal{O}(\lambda)]. \end{aligned}$$

Using the expansion $\frac{1}{1+x} = 1 - x + x^2 - x^3 + \dots$ with $x = \mathcal{O}(\lambda)$,

$$E_n - E_m^{(0)} = \left(E_n^{(0)} - E_m^{(0)} \right) \frac{1}{1 - \mathcal{O}(\lambda)}$$

and plugging this in to (5) we get

$$\begin{aligned}\langle \psi_m^{(0)} | \psi_n \rangle &= \frac{\lambda \langle \psi_m^{(0)} | H' \left(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \mathcal{O}(\lambda^2) \right)}{E_n^{(0)} - E_m^{(0)}} [1 + \mathcal{O}(\lambda^2)] \\ &= \frac{\lambda \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} + \mathcal{O}(\lambda^2),\end{aligned}\quad n \notin D_n. \quad (6)$$

If instead $m \in D_n$ then

$$\begin{aligned}E_n - E_m^{(0)} &= \left(E_n^{(0)} - E_m^{(0)} \right) + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \mathcal{O}(\lambda^3) \\ &= \lambda E_n^{(1)} \left(1 + \lambda \left[\frac{E_n^{(2)}}{E_n^{(1)}} + \mathcal{O}(\lambda) \right] \right)\end{aligned}$$

Again, we use the expansion $\frac{1}{1+x} = 1 - x + x^2 - x^3 + \dots$, but now with $x = \lambda \left[\frac{E_n^{(2)}}{E_n^{(1)}} + \mathcal{O}(\lambda) \right]$. We get

$$E_n - E_m^{(0)} = \left(E_n^{(0)} - E_m^{(0)} \right) + \frac{\lambda E_n^{(1)}}{1 - \lambda \frac{E_n^{(2)}}{E_n^{(1)}} + \mathcal{O}(\lambda^2)}.$$

Plugging this in to (5) we get

$$\begin{aligned}\langle \psi_m^{(0)} | \psi_n \rangle &= \frac{\langle \psi_m^{(0)} | H' \left(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \mathcal{O}(\lambda^2) \right)}{E_n^{(1)}} \left[1 - \lambda \frac{E_n^{(2)}}{E_n^{(1)}} + \mathcal{O}(\lambda^2) \right] \\ &= \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(1)}} + \lambda \left[\frac{\langle \psi_m^{(0)} | H' | \psi_n^{(1)} \rangle}{E_n^{(1)}} - \frac{E_n^{(2)} \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{[E_n^{(1)}]^2} \right] + \mathcal{O}(\lambda^2), \quad n \in D_n.\end{aligned}\quad (7)$$

Now, we can write an expression for complete state. We have $|\psi_n\rangle = \sum_m |\psi_m^{(0)}\rangle \langle \psi_m^{(0)} | \psi_n \rangle$ and we can read off the $\langle \psi_m^{(0)} | \psi_n \rangle$ from (6) and (7). Putting this all together,

$$\begin{aligned}|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \mathcal{O}(\lambda^2) &= \sum_{m \in D_n} |\psi_m^{(0)}\rangle \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(1)}} \\ &\quad + \lambda \left\{ \sum_{m \in D_n} |\psi_m^{(0)}\rangle \left[\frac{\langle \psi_m^{(0)} | H' | \psi_n^{(1)} \rangle}{E_n^{(1)}} - \frac{E_n^{(2)} \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{[E_n^{(1)}]^2} \right] \right. \\ &\quad \left. + \sum_{m \notin D_n} |\psi_m^{(0)}\rangle \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \right\} \\ &\quad + \mathcal{O}(\lambda^2).\end{aligned}\quad (8)$$

Equating orders of λ , we have a zero-order equation

$$\boxed{|\psi_n^{(0)}\rangle = \sum_{m \in D_n} |\psi_m^{(0)}\rangle \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(1)}}} \quad (9)$$

and a first-order equation

$$\boxed{\left| \psi_n^{(1)} \right\rangle = \sum_{m \in D_n} \left| \psi_m^{(0)} \right\rangle \left[\frac{\langle \psi_m^{(0)} | H' | \psi_n^{(1)} \rangle}{E_n^{(1)}} - \frac{E_n^{(2)} \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{[E_n^{(1)}]^2} \right] + \sum_{m \notin D_n} \left| \psi_m^{(0)} \right\rangle \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}.} \quad (10)$$

1(a).4 First order energy

Multiplying (9) by $\langle \psi_n^{(0)} |$,

$$\begin{aligned} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle &= \sum_{m \in D_n} \langle \psi_n^{(0)} | \psi_m^{(0)} \rangle \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(1)}} \\ 1 &= \sum_{m \in D_n} \delta_{mn} \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(1)}} \end{aligned}$$

so

$$\boxed{E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle.}$$

In words, the first order energy correction is the expectation value of H' for the zero-order state.

2 Identical particles

Suppose we have a system of two identical particles with the wavefunction $\Psi(x_1, x_2)$ where x_1 and x_2 are coordinates of the particles (taking into account things like position and spin).

Fact of Nature 1. *Particles either have wavefunctions that are symmetric, with $\Psi(x_1, x_2) = \Psi(x_2, x_1)$, or antisymmetric, with $\Psi(x_1, x_2) = -\Psi(x_2, x_1)$.*

We call the symmetric type of particles bosons and the antisymmetric type of particles fermions.

2(a) Pauli exclusion principle

Consider a wavefunction $\Psi(x_1, x_2)$ for two fermions. If $x_1 = x_2 = x$ then we have $\Psi(x, x) = -\Psi(x, x)$ so it must be that $\Psi(x, x) = 0$. This shows that two identical fermions cannot occupy the same state.

3 Time-dependent perturbation theory in the interaction picture

Perturbation theory setup. 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

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

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,

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

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.

$$\begin{aligned} \int_{t_0}^t \frac{\partial}{\partial t'} |\Psi_I, t'\rangle &= -\frac{i}{\hbar} \int_{t_0}^t \hat{H}_I(t') |\Psi_I, t'\rangle dt' \\ |\Psi_I, t\rangle - |\Psi_I, t_0\rangle &= -\frac{i}{\hbar} \int_{t_0}^t \hat{H}_I(t') |\Psi_I, t'\rangle dt' \\ |\Psi_I, t\rangle &= |\Psi_I, t_0\rangle - \frac{i}{\hbar} \int_{t_0}^t \hat{H}_I(t') |\Psi_I, t'\rangle dt' \end{aligned} \tag{11}$$

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

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

Plugging this in for the state inside the integral in (11), we get the first order approximation

$$|\Psi_I, t\rangle = |\Psi_I, t_0\rangle - \frac{i}{\hbar} \int_{t_0}^t \hat{H}_I(t') |\Psi_I, t_0\rangle dt' + \mathcal{O}(\hat{H}_I(t)^2). \quad (12)$$

We can plug in again to get the second order approximation

$$|\Psi_I, t\rangle = |\Psi_I, t_0\rangle - \frac{i}{\hbar} \int_{t_0}^t \hat{H}_I(t') \left[|\Psi_I, t_0\rangle - \frac{i}{\hbar} \int_{t_0}^{t'} \hat{H}_I(t'') |\Psi_I, t_0\rangle dt'' \right] dt' + \mathcal{O}(\hat{H}_I(t)^3).$$

In general, we can keep going to achieve higher order approximations. For us, however, the first order approximation (12) is enough.

Application to 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

$$\langle x_1, x_2 | \hat{V}(t) | \psi \rangle = \int_{x_1, x_2} \frac{d^3 x_1 d^3 x_2}{(2\pi)^6} V(x_1 - x_2) \langle x_1, x_2 | \psi \rangle.$$

(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

$$\langle x_1, x_2 | k_1, k_2 \rangle = e^{ik_1 \cdot x_1 + ik_2 \cdot x_2}.$$

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 $\frac{1}{2m} (k_1^2 + k_2^2)$ and so

$$\hat{U}(t_0, t) |k_1, k_2\rangle = e^{\frac{i(t-t_0)(k_1^2 + k_2^2)}{2m\hbar}} |k_1, k_2\rangle. \quad (13)$$

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

$$V(x_1 - x_2) = \int_{-\infty}^{\infty} \frac{d^3 p}{(2\pi)^3} \tilde{V}(p) e^{ip \cdot (x_1 - x_2)}. \quad (14)$$

We now consider (12) and take the limits $t_0 \rightarrow -\infty$ and $t \rightarrow \infty$ 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 $\langle k'_1, k'_2|$,

$$\begin{aligned} \langle k'_1, k'_2 | \Psi_I, \infty \rangle &= \langle k'_1, k'_2 | k_1, k_2 \rangle - \frac{i}{\hbar} \int_{-\infty}^{\infty} \langle k'_1, k'_2 | \hat{H}_I(t) | k_1, k_2 \rangle dt \\ &= \delta^3(k'_1 - k_1) \delta^3(k'_2 - k_2) - \frac{i}{\hbar} \int_{-\infty}^{\infty} \langle k'_1, k'_2 | \hat{H}_I(t) | k_1, k_2 \rangle dt. \end{aligned} \quad (15)$$

This motivates us to compute the matrix element

$$\langle k'_1, k'_2 | \hat{H}_I(t) | k_1, k_2 \rangle = \langle k'_1, k'_2 | \hat{U}(t_0, t)^\dagger \hat{V}(t) \hat{U}(t_0, t) | k_1, k_2 \rangle.$$

Plugging in (13),

$$\begin{aligned}
\langle k'_1, k'_2 | \hat{H}_I(t) | k_1, k_2 \rangle &= \langle k'_1, k'_2 | e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2)}{2m\hbar}} \hat{V}(t) e^{-\frac{i(t-t_0)(k_1^2 + k_2^2)}{2m\hbar}} | k_1, k_2 \rangle \\
&= e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \langle k'_1, k'_2 | \hat{V}(t) | k_1, k_2 \rangle \\
&= e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \langle k'_1, k'_2 | \left\{ \int_{x_1, x_2} \frac{d^3 x_1 d^3 x_2}{(2\pi)^6} | x_1, x_2 \rangle \langle x_1, x_2 | \right\} \hat{V}(t) | k_1, k_2 \rangle \\
&= e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \int_{x_1, x_2} \frac{d^3 x_1 d^3 x_2}{(2\pi)^6} \langle k'_1, k'_2 | x_1, x_2 \rangle \langle x_1, x_2 | \hat{V}(t) | k_1, k_2 \rangle \\
&= e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \int_{x_1, x_2} \frac{d^3 x_1 d^3 x_2}{(2\pi)^6} e^{-ik'_1 \cdot x_1 - ik'_2 \cdot x_2} V(x_1 - x_2) e^{ik_1 \cdot x_1 + ik_2 \cdot x_2}
\end{aligned}$$

and plugging in (14),

$$\begin{aligned}
\langle k'_1, k'_2 | \hat{H}_I(t) | k_1, k_2 \rangle &= e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \int_{-\infty}^{\infty} \frac{d^3 p}{(2\pi)^3} \int_{x_1, x_2} \frac{d^3 x_1 d^3 x_2}{(2\pi)^6} e^{-ik'_1 \cdot x_1 - ik'_2 \cdot x_2} \tilde{V}(p) e^{ip \cdot (x_1 - x_2)} e^{ik_1 \cdot x_1 + ik_2 \cdot x_2} \\
&= e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \int_{-\infty}^{\infty} \frac{d^3 p}{(2\pi)^3} \tilde{V}(p) \int_{x_1, x_2} \frac{d^3 x_1 d^3 x_2}{(2\pi)^6} e^{i(k_1 - k'_1 + p) \cdot x_1} e^{i(k_2 - k'_2 - p) \cdot x_2} \\
&= e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \int_{-\infty}^{\infty} \frac{d^3 p}{(2\pi)^3} \tilde{V}(p) \delta^3(k_1 - k'_1 + p) \delta^3(k_2 - k'_2 - p) \\
&= e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \tilde{V}(k'_1 - k_1) \delta^3(k'_1 - k_1 - k'_2 + k_2).
\end{aligned}$$

Putting this in to (15) we get

$$\begin{aligned}
\langle k'_1, k'_2 | \Psi_I, \infty \rangle &= \delta^3(k'_1 - k_1) \delta^3(k'_2 - k_2) - \frac{i}{\hbar} \int_{-\infty}^{\infty} dt e^{\frac{i(t-t_0)(k_1'^2 + k_2'^2 - k_1^2 - k_2^2)}{2m\hbar}} \tilde{V}(k'_1 - k_1) \delta^3(k'_1 - k_1 - k'_2 + k_2) \\
&= \delta^3(k'_1 - k_1) \delta^3(k'_2 - k_2) \\
&\quad - i \tilde{V}(k'_1 - k_1) \delta^3(k'_1 - k_1 - k'_2 + k_2) \delta \left(\frac{1}{2m} (k_1'^2 + k_2'^2 - k_1^2 - k_2^2) \right). \quad (16)
\end{aligned}$$

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

Mixed states and the density operator. We now consider the same problem but where we allow for mixed states. We will need to describe the system by the density operator $\hat{\rho}(t)$. First, let us derive the time evolution of $\hat{\rho}(t)$ in first order perturbation theory.

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

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

At time t states will have evolved according to (12), so

$$\hat{\rho}(t) = \sum_n P_n |\psi_{I_n}, t\rangle \langle \psi_{I_n}, t|$$

where

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

so

$$\hat{\rho}(t) = \hat{\rho}(t_0) - \frac{i}{\hbar} \int_{t_0}^t \left[\hat{H}_I(t'), \hat{\rho}(t_0) \right] dt' + \mathcal{O}(\hat{H}_I(t)^2). \quad (17)$$

As before, we drop the higher order terms and take $t \rightarrow \infty$ and $t_0 \rightarrow -\infty$. Then the momentum basis amplitude is

$$\langle k_1', k_2' | \hat{\rho}(t) | k_1, k_2 \rangle$$