Quantum mechanics II, Problems 14 : Time-Dependent Perturbation Theory

Solutions

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Problem 1 : Time-dependent Perturbation Theory - Perturbed Harmonic Oscillator

Let's consider a harmonic oscillator described by

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \tag{1}$$

on which a sudden electric field $\hat{V} = -F\hat{x}$ is suddenly applied.

1. Determine the exact transition probability $P_{\psi_0^{(0)} \to \psi_n}$ between an initial state (ground state of $\hat{H}_0$) and an excited state (exited state of $\hat{H} = \hat{H}_0 + \hat{V}$) following this perturbation.
   The trick of this exercise is to notice that $\hat{V}_{tot} = \frac{m\omega^2}{2}\hat{x}^2 - F\hat{x}$ can be written as

$$V_{tot}(x) = \frac{m\omega^2}{2}(x - x_0)^2 + \text{Const.} \tag{2}$$

   We can then deduce that the perturbed wave functions $\psi_n(x)$ will simply be the unperturbed wave functions $\psi_n^{(0)}(x)$ shifted by :

$$x_0 = \frac{F}{m\omega^2}. \tag{3}$$

   that is $\psi_n(x) = \psi_n^{(0)}(x - x_0)$. The goal here is to calculate $\left|\left\langle \psi_0^{(0)} \middle| \psi_n \right\rangle\right|^2$, where $\left|\psi_0^{(0)}(x)\right\rangle$ is the unperturbed ground state, and $\psi_n(x) = \psi_n^{(0)}(x - x_0)$ is the n-th excited state of the perturbed harmonic oscillator. The eigenstates of the system are well-known and we have in particular :

$$\psi_0^{(0)}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \mathrm{e}^{-\frac{m\omega}{2\hbar}x^2} \tag{4}$$

$$\psi_n^{(0)}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \mathrm{e}^{-\frac{m\omega}{2\hbar}x^2} H_n\left(x\sqrt{\frac{m\omega}{\hbar}}\right) \tag{5}$$

   with :

$$H_n(y) = (-1)^n \mathrm{e}^{y^2} \frac{d^n \mathrm{e}^{-y^2}}{\mathrm{d}y^n}. \tag{6}$$

Ergo we calculate

$$\left\langle \psi_0^{(0)} \middle| \psi_n \right\rangle = \int_{-\infty}^{\infty} \psi_0^{(0)}(x)^* \, \psi_n(x) \, \mathrm{d}x = \int_{-\infty}^{\infty} \psi_0^{(0)}(x)^* \, \psi_n^{(0)}(x - x_0) \, \mathrm{d}x \tag{7}$$

$$= \int_{-\infty}^{\infty} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \mathrm{e}^{-\frac{m\omega}{2\hbar}x^2} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \mathrm{e}^{-\frac{m\omega}{2\hbar}(x-x_0)^2} H_n\left((x - x_0)\sqrt{\frac{m\omega}{\hbar}}\right)$$

$$= \frac{1}{\sqrt{2^n n!}} \frac{1}{\sqrt{\pi}} \sqrt{\frac{m\omega}{\hbar}} \int_{-\infty}^{\infty} \mathrm{e}^{-\frac{m\omega}{2\hbar}\left(2x^2 - 2x\,x_0 + x_0{}^2\right)} H_n\left((x - x_0)\sqrt{\frac{m\omega}{\hbar}}\right) \mathrm{d}x. \tag{8}$$

To make this a little prettier, we introduce a change of variables $y = x\sqrt{\frac{m\omega}{\hbar}}$, such that $\mathrm{d}x = \mathrm{d}y\sqrt{\frac{\hbar}{m\omega}}$ and $x^2 = y^2 \frac{\hbar}{m\omega}$. We similarly define constant $y_0 = x_0\sqrt{\frac{m\omega}{\hbar}}$, so that our integral simplifies to

$$\left\langle \psi_0^{(0)} \middle| \psi_n \right\rangle = \frac{1}{\sqrt{\pi 2^n n!}} \int_{-\infty}^{\infty} \mathrm{e}^{-y^2 + y\,y_0 - \frac{1}{2}y_0{}^2} H_n\left(y - y_0\right) \mathrm{d}y. \tag{9}$$

We now substitute our given form of the Hermite polynomial, taking care to differentiate *then* substitute $y - y_0$ as the argument.

$$= \frac{1}{\sqrt{\pi 2^n n!}} \int_{-\infty}^{\infty} \mathrm{e}^{-y^2 + y\,y_0 - \frac{1}{2}y_0{}^2} (-1)^n \mathrm{e}^{(y-y_0)^2} \left(\frac{\mathrm{d}^n \mathrm{e}^{-z^2}}{\mathrm{d}z^n}\right)_{z \to y - y_0} \mathrm{d}y \tag{10}$$

$$= \frac{(-1)^n \, e^{y_0{}^2/2}}{\sqrt{\pi 2^n n!}} \int_{-\infty}^{\infty} \mathrm{e}^{-y\,y_0} \left(\frac{\mathrm{d}^n \mathrm{e}^{-z^2}}{\mathrm{d}z^n}\right)_{z \to y - y_0} \mathrm{d}y \tag{11}$$

To proceed, we must recognise that

$$\left(\frac{\mathrm{d}^n \mathrm{e}^{-z^2}}{\mathrm{d}z^n}\right)_{z \to y - y_0} = \frac{\mathrm{d}^n}{\mathrm{d}y^n} e^{-(y-y_0)^2} \tag{12}$$

which you can either intuit, or prove by induction. Our integral is now

$$\left\langle \psi_0^{(0)} \middle| \psi_n \right\rangle = \frac{(-1)^n \, e^{y_0{}^2/2}}{\sqrt{\pi 2^n n!}} \int_{-\infty}^{\infty} \mathrm{e}^{-y\,y_0} \frac{\mathrm{d}^n}{\mathrm{d}y^n} e^{-(y-y_0)^2} \mathrm{d}y \tag{13}$$

$$= \frac{(-1)^n \, e^{-y_0{}^2/2}}{\sqrt{\pi 2^n n!}} \int_{-\infty}^{\infty} \mathrm{e}^{-y\,y_0} \frac{\mathrm{d}^n}{\mathrm{d}y^n} e^{-y^2 + 2y\,y_0} \mathrm{d}y \tag{14}$$

We can evaluate this by repeatedly invoking integration by parts, using

$$\int_a^b u \frac{\mathrm{d}v}{\mathrm{d}y} \, \mathrm{d}y = \left[u\,v\right]_a^b - \int_a^b \frac{\mathrm{d}u}{\mathrm{d}y} \, v \, \mathrm{d}y \tag{15}$$

where $u = e^{-yy_0}$ and (for the first invocation) $\frac{\mathrm{d}v}{\mathrm{d}y} = \frac{\mathrm{d}}{\mathrm{d}y}\frac{\mathrm{d}^{n-1}}{\mathrm{d}y^{n-1}}e^{-y^2+2y\,y_0}$. A single invocation produces

$$\int_{-\infty}^{\infty} \mathrm{e}^{-y\,y_0}\frac{\mathrm{d}^n}{\mathrm{d}y^n}e^{-y^2+2y\,y_0}\mathrm{d}y = \left[\mathrm{e}^{-y\,y_0}\frac{\mathrm{d}^{n-1}}{\mathrm{d}y^{n-1}}e^{-y^2+2y\,y_0}\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty}(-y_0)\mathrm{e}^{-y\,y_0}\frac{\mathrm{d}^{n-1}}{\mathrm{d}y^{n-1}}e^{-y^2+2y\,y_0}.\mathrm{d}y \tag{16}$$

We next realise that $\frac{\mathrm{d}^{n-1}}{\mathrm{d}y^{n-1}}e^{-y^2+2y\,y_0} = P(y)e^{-y^2+2y\,y_0}$ where P is a polynomial, and ergo that the left term above vanishes at both end-points :

$$\lim_{y\to\pm\infty}\mathrm{e}^{-y\,y_0}\frac{\mathrm{d}^{n-1}}{\mathrm{d}y^{n-1}}e^{-y^2+2y\,y_0} = \lim_{y\to\pm\infty}P(y)\,e^{-y^2+y\,y_0} = 0, \tag{17}$$

since y^2 dominates y, and since the exponentials dominate polynomials. We have shown that

$$\int_{-\infty}^{\infty}\mathrm{e}^{-y\,y_0}\frac{\mathrm{d}^n}{\mathrm{d}y^n}e^{-y^2+2y\,y_0}\mathrm{d}y = y_0\int_{-\infty}^{\infty}\mathrm{e}^{-y\,y_0}\frac{\mathrm{d}^{n-1}}{\mathrm{d}y^{n-1}}e^{-y^2+2y\,y_0}\mathrm{d}y, \tag{18}$$

making it clear that repeating integration by parts a total of n times yields

$$= {y_0}^n\int_{-\infty}^{\infty}\mathrm{e}^{-y\,y_0}\frac{\mathrm{d}^0}{\mathrm{d}y^0}e^{-y^2+2y\,y_0}\mathrm{d}y = {y_0}^n\int_{-\infty}^{\infty}e^{-y^2+y\,y_0}\mathrm{d}y \tag{19}$$

which finally, by "completing the square" in the exponent, we recognise as a standard integral ; that of the error function, shifted, which makes no difference across our infinite domain.

$$= {y_0}^n\,e^{\frac{{y_0}^2}{4}}\int_{-\infty}^{\infty}e^{-(y-y_0/2)^2}\mathrm{d}y = {y_0}^n\,e^{\frac{{y_0}^2}{4}}\int_{-\infty}^{\infty}e^{-y^2}\mathrm{d}y = {y_0}^n\,e^{\frac{{y_0}^2}{4}}\,\sqrt{\pi}. \tag{20}$$

We have ergo shown

$$\left\langle\psi_0^{(0)}\middle|\psi_n\right\rangle = \frac{(-1)^n\,e^{-{y_0}^2/2}}{\sqrt{\pi 2^n n!}}\,{y_0}^n\,e^{\frac{{y_0}^2}{4}}\,\sqrt{\pi} = \frac{(-1)^n\,e^{-{y_0}^2/4}}{\sqrt{2^n n!}}\,{y_0}^n, \tag{21}$$

and so the transition probability is

$$P_{\psi_0^{(0)}\to\psi_n} = \left|\left\langle\psi_0^{(0)}\middle|\psi_n\right\rangle\right|^2 = \frac{e^{-{y_0}^2/2}}{2^n\,n!}{y_0}^{2n} \equiv \frac{\lambda^n}{n!}e^{-\lambda}, \tag{22}$$

where $\lambda = \frac{1}{2}{y_0}^2 = \frac{F^2}{2\,m\,\hbar\,\omega^3}$. We recognise this as a Poisson distribution with parameter λ. Note that this probability does not depend on time as we are interested in the transition probability between an eigenstate of the unperturbed system and an eigenstate of the perturbed system :

$$P_{\psi_0^{(0)}\to\psi_n} = \left|\left\langle\psi_n\middle|\hat{U}(t)\middle|\psi_0^{(0)}\right\rangle\right|^2 = \left|\mathrm{e}^{itE_n/\hbar}\left\langle\psi_n\middle|\psi_0^{(0)}\right\rangle\right|^2 = \left|\left\langle\psi_n\middle|\psi_0^{(0)}\right\rangle\right|^2 \tag{23}$$

2. Under what condition does $\hat{V}$ correspond to a weak perturbation ? In this limit, determine $P_{\psi_0^{(0)}\to\psi_1}$.
   The theory of perturbations is applicable if $z \ll 1$. In this case, the dominant transition is obviously the one to the first excited state, namely $P_{\psi_0^{(0)}\to\psi_1} \approx z$.

3. Find the expression of $P_{\psi_0^{(0)}\to\psi_1}$ using first-order time-dependent perturbation theory and compare it to the previous result.

To analyze the problem with time-dependent perturbation theory, we can first rewrite $\hat{V}$ as a function of time using the Heaviside function (to model the sudden application of $\hat{V}$)) :

$$\hat{V}(t) := \hat{V}\,\theta(t-t_0) = -\theta(t-t_0)F\hat{x}. \tag{24}$$

Furthermore, we can admit without loss of generality that $t_0 = 0$. The idea is to calculate the transition probability just after the application of the perturbation :

$$\left|\left\langle \psi_1 \left| \lim_{t\to t_0^+} \hat{U}_I(t,t_0) \right| \psi_0^{(0)} \right\rangle\right|^2 \tag{25}$$

$$= \left|\left\langle \psi_1 \left| \lim_{t\to t_0^+} \left(\mathbb{1} - \frac{i}{\hbar}\int_{-\infty}^{t} e^{i\hat{H}_0 t'/\hbar}\hat{V}e^{-iE_0^{(0)}t'/\hbar}\theta(t'-t_0)\,\mathrm{d}t' \right) \right| \psi_0^{(0)} \right\rangle\right|^2 \tag{26}$$

$$= \left|\left\langle \psi_1 | \psi_0^{(0)} \right\rangle - \frac{i}{\hbar}\lim_{t\to t_0^+}\int_{t_0}^{t}\left\langle \psi_1 \left| e^{i\hat{H}_0 t'/\hbar}\hat{V}e^{-iE_0^{(0)}t'/\hbar} \right| \psi_0^{(0)} \right\rangle \mathrm{d}t' \right|^2 . \tag{27}$$

Now, let us rewrite $|\psi_1\rangle$ in the eigenbasis of $\hat{H}_0$ as $|\psi_1\rangle = \sum_{k\geq 0} a_k |\psi_k^{(0)}\rangle$, and we also define $\omega_{ij} = (E_i^{(0)} - E_j^{(0)})/\hbar$ for simplicity. Therefore, in previous equation we need to compute the following terms (for all $k \geq 0$) :

$$\lim_{t\to t_0^+}\int_{t_0}^{t}\left\langle \psi_k^{(0)} \left| e^{i\hat{H}_0 t'/\hbar}\hat{V}e^{-iE_0^{(0)}t'/\hbar} \right| \psi_0^{(0)} \right\rangle \mathrm{d}t' = \left\langle \psi_k^{(0)} \left| \hat{V} \right| \psi_0^{(0)} \right\rangle \underbrace{\lim_{t\to t_0^+}\int_{t_0}^{t} e^{i\omega_{k0}t'}\,\mathrm{d}t'}_{=0} . \tag{28}$$

Notice that $\lim_{t\to t_0^+}\int_{t_0}^{t} e^{i\omega_{k0}t'}\,\mathrm{d}t'$ vanishes for any $k \geq 0$ as for $k = 0$, we have $\int_{t_0}^{t} e^{i\omega_{k0}t'}\,\mathrm{d}t' = t - t_0$, and for $k > 0$ we have $\int_{t_0}^{t} e^{i\omega_{k0}t'}\,\mathrm{d}t' = (e^{i\omega_{k0}t} - e^{i\omega_{k0}t_0})/(i\omega_{k0})$ with $\omega_{k0} \neq 0$. Therefore, the limit of the integral in Eq. (27) vanishes, which leads to

$$\left|\left\langle \psi_1 \left| \lim_{t\to t_0^+} \hat{U}_I(t,t_0) \right| \psi_0^{(0)} \right\rangle\right|^2 = \left|\left\langle \psi_1 | \psi_0^{(0)} \right\rangle\right|^2 . \tag{29}$$

We thus recover Eq. (23) from first-order time-dependent perturbation theory.

<u>*Note :*</u> Let's calculate - although not necessary - the matrix element $V_{10} := \langle \psi_1 | V(x) \rangle\, \psi_0^{(0)}$. First, let's recall that

$$x = \frac{1}{\sqrt{2}}\sqrt{\frac{\hbar}{m\omega}}(a^\dagger + a), \tag{30}$$

and we also know that

$$\begin{aligned} \psi_0^{(0)}(x) &= \langle x | 0 \rangle , \\ \psi_1^{(0)}(x) &= \left\langle x \right| a^\dagger \left| 0 \right\rangle . \end{aligned} \tag{31}$$

The perturbed state $\psi_1(x)$, in terms of the unperturbed states, can be written as a linear combination of $\psi_n^{(0)}(x)$ (i.e., $\psi_1(x - x_0) = \sum_n a_n \psi_n^{(0)}(x)$). We can therefore conclude that the only non-zero term in V_{10} is given by

$$V_{10} = a_1 \int_{-\infty}^{\infty} \psi_1^{*(0)}(x) F x \psi_0^{(0)}(x) \mathrm{d}x \tag{32}$$

$$= a_1 \frac{m\omega}{\hbar} \sqrt{\frac{2}{\pi}} F \int_{-\infty}^{\infty} x^2 \mathrm{e}^{-\frac{m\omega}{\hbar}x^2} \mathrm{d}x \tag{33}$$

$$= a_1 F \frac{1}{\sqrt{2}} \sqrt{\frac{\hbar}{m\omega}}, \tag{34}$$

where $a_1 = \int\limits_{-\infty}^{\infty} \psi_1^{(0)*} \psi_1 \mathrm{d}x$.

Problem 2 : Two degenerate states

Let's consider a system described by a Hamiltonian $\hat{H}_0$ with 2 eigenstates $\psi_1^{(0)}$ and $\psi_2^{(0)}$ having the same energy E. We perturb the system as follows : $\hat{H} = \hat{H}_0 + \hat{V}$.

1. At first order according to perturbation theory, the eigenstates become :

$$\psi^{(0)} = c_1^{(0)} \psi_1^{(0)} + c_2^{(0)} \psi_2^{(0)} \quad \text{and} \quad \psi'^{(0)} = c_1'^{(0)} \psi_1^{(0)} + c_2'^{(0)} \psi_2^{(0)} \tag{35}$$

What are the values of coefficients $c_{1,2}^{(0)}$ and $c_{1,2}'^{(0)}$?

Here we consider 2 degenerate levels. Perturbation theory tells us to diagonalize the matrix $\hat{V}$ by defining its elements V_{ij} where $\{i, j\} \in \{1, 2\}$ in order to determine the first-order energy correction. We easily find :

$$E^{(1)} = \frac{1}{2}\left(V_{11} + V_{22} + \hbar\omega^{(1)}\right) \tag{36}$$

$$E'^{(1)} = \frac{1}{2}\left(V_{11} + V_{22} - \hbar\omega^{(1)}\right) \tag{37}$$

with the definition :

$$\hbar\omega^{(1)} := \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}. \tag{38}$$

the corresponding coefficients of the normalized eigenvectors are :

$$c_1^{(0)} = \frac{V_{12}}{\sqrt{\hbar\omega^{(1)}\left(\frac{\hbar\omega^{(1)}}{2} \pm \frac{(V_{22}-V_{11})}{2}\right)}} e^{i\phi_\pm} \tag{39}$$

$$c_2^{(0)} = \pm\sqrt{\frac{\frac{\hbar\omega^{(1)}}{2} \pm \frac{(V_{22}-V_{11})}{2}}{\hbar\omega^{(1)}}} e^{i\phi_\pm}, \tag{40}$$

which are valid for any phases $\phi_\pm \in \mathbb{R}$. For example, one could use $e^{i\phi_\pm} = \sqrt{\frac{V_{21}}{|V_{12}|}}$ to get (solutions from previous years) :

$$c_1^{(0)} = \sqrt{\frac{V_{12}}{2|V_{12}|}\left(1 \pm \frac{V_{11} - V_{22}}{\hbar\omega^{(1)}}\right)} \tag{41}$$

$$c_2^{(0)} = \pm\sqrt{\frac{V_{21}}{2|V_{12}|}\left(1 \mp \frac{V_{11} - V_{22}}{\hbar\omega^{(1)}}\right)}. \tag{42}$$

2. If the initial state is $\psi_1^{(0)}$, what is the probability of finding the system in state $\psi_2^{(0)}$ at time t ? Show that for short times we obtain :

$$P_{1\to 2}(t) = \frac{t^2}{\hbar^2}|V_{21}|^2. \tag{43}$$

Going from expressions :

$$\left|\psi^{(0)}\right\rangle = c_1^{(0)}\left|\psi_1^{(0)}\right\rangle + c_2^{(0)}\left|\psi_2^{(0)}\right\rangle \tag{44}$$
$$\left|\psi'^{(0)}\right\rangle = c_1'^{(0)}\left|\psi_1^{(0)}\right\rangle + c_2'^{(0)}\left|\psi_2^{(0)}\right\rangle \tag{45}$$

which we can use to get $\psi_1^{(0)}$ as a function of non-disturbed eigenstates :

$$\left|\psi_1^{(0)}\right\rangle = \frac{c_2'^{(0)}\left|\psi^{(0)}\right\rangle - c_2^{(0)}\left|\psi'^{(0)}\right\rangle}{c_1^{(0)}c_2'^{(0)} - c_1'^{(0)}c_2^{(0)}}, \tag{46}$$

and so at time t applying the evolution operator $\hat{U}(t)\left|\psi_1^{(0)}\right\rangle$, each eigenstates evolves of course at its own frequency :

$$\left|\psi_1^{(0)}(t)\right\rangle = \mathrm{e}^{-\frac{i}{\hbar}Et}\frac{c_2'^{(0)}\mathrm{e}^{-\frac{i}{\hbar}E^{(1)}t}\left|\psi^{(0)}\right\rangle - c_2^{(0)}\mathrm{e}^{-\frac{i}{\hbar}E'^{(1)}t}\left|\psi'^{(0)}\right\rangle}{c_1^{(0)}c_2'^{(0)} - c_1'^{(0)}c_2^{(0)}}. \tag{47}$$

and the frequency associated with $\hat{H}_0$ introduces a global phase factor. Now we seek the probability of being in state $\left|\psi_2^{(0)}\right\rangle$ at time t, so it is necessary to rework with the eigenstates by reintroducing (44, 45) into (47), and we take the inner product with

$$\left|\psi_2^{(0)}\right\rangle = \frac{-c_1'^{(0)}\left|\psi^{(0)}\right\rangle + c_1^{(0)}\left|\psi'^{(0)}\right\rangle}{c_1^{(0)}c_2'^{(0)} - c_1'^{(0)}c_2^{(0)}}, \tag{48}$$

to find the probability :

$$P_{1\to 2}(t) = \left|\left\langle\psi_2^{(0)}\middle|\psi_1^{(0)}(t)\right\rangle\right|^2 = \frac{4|V_{21}|^2}{(\hbar\omega^{(1)})^2}\sin^2\left(\frac{\omega^{(1)}t}{2}\right) \tag{49}$$
$$= \frac{2|V_{21}|^2}{(\hbar\omega^{(1)})^2}\left[1-\cos\left(\omega^{(1)}t\right)\right]. \tag{50}$$

The excitation probability oscillates at frequency $\omega^{(1)}$, and in other words, the system oscillates between its 2 eigenstates. In the case $t\omega^{(1)} \ll 1$, $P_{1\to 2}(t)$ reduces to :

$$P_{1\to 2}(t) = \frac{t^2}{\hbar^2}|V_{21}|^2 \tag{51}$$

by expanding the cosine to second order.

3. Retrieve the result (43) through time-dependent perturbation theory.
With a first-order expansion of $\mathrm{e}^{it\hat{H}/\hbar}$ in t to immediately recover :

$$\left\langle \psi_2^{(0)} \right| \hat{U}(t) \left| \psi_1^{(0)} \right\rangle = \left\langle \psi_2^{(0)} \right| \mathrm{e}^{it\hat{H}/\hbar} \left| \psi_1^{(0)} \right\rangle = \left\langle \psi_2^{(0)} \right| 1 + it\hat{H}/\hbar \left| \psi_1^{(0)} \right\rangle \tag{52}$$

$$= \frac{it}{\hbar} \left\langle \psi_2^{(0)} \right| \hat{H}_0 + \hat{V} \left| \psi_1^{(0)} \right\rangle = \frac{it}{\hbar} \left\langle \psi_2^{(0)} \right| \hat{V} \left| \psi_1^{(0)} \right\rangle \tag{53}$$

since $\left\langle \psi_2^{(0)} \right| \hat{H}_0 \left| \psi_1^{(0)} \right\rangle = E \left\langle \psi_2^{(0)} \middle| \psi_1^{(0)} \right\rangle = 0$. We then find :

$$P_{1\to 2}(t) = \frac{t^2}{\hbar^2} |V_{21}|^2. \tag{54}$$