

## 22.5.3: iii. Exercise Solutions

### Q1

a. Evaluate the z-component of  $\mu_{fi}$ :

$$\mu_{fi} = \langle 2p_z | e r \cos \theta | 1s \rangle, \text{ where } \psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}, \text{ and } \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{\frac{5}{2}} r \cos \theta e^{-\frac{Zr}{2a_0}} \quad (22.5.3.1)$$

$$\mu_{fi} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{\frac{5}{2}} \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \langle r \cos \theta e^{-\frac{Zr}{2a_0}} | e r \cos \theta | e^{-\frac{Zr}{a_0}} \rangle \quad (22.5.3.2)$$

$$= \frac{e}{4\pi\sqrt{2}} \left( \frac{Z}{a_0} \right)^4 \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi \left( r^2 e^{-\frac{Zr}{2a_0}} e^{-\frac{Zr}{a_0}} \right) \cos^2 \theta \quad (22.5.3.3)$$

$$= \frac{e}{4\pi\sqrt{2}} 2\pi \left( \frac{Z}{a_0} \right)^4 \int_0^\infty \left( r^4 e^{-\frac{3Zr}{2a_0}} \right) dr \int_0^\pi \sin \theta \cos^2 \theta d\theta \quad (22.5.3.4)$$

Using integral equation 4 to integrate over r and equation 17 to integrate over  $\theta$  we obtain:

$$= \frac{e}{4\pi\sqrt{2}} 2\pi \left( \frac{Z}{a_0} \right)^4 \frac{4}{\left( \frac{3Z}{2a_0} \right)^5} \left( \frac{-1}{3} \right) \cos^3 \theta \Big|_0^\pi \quad (22.5.3.5)$$

$$= \frac{e}{4\pi\sqrt{2}} 2\pi \left( \frac{Z}{a_0} \right)^4 \frac{2^5 a_0^5}{3^5 Z^5} \left( \frac{-1}{3} \right) ((-1)^3 - (1)^3) \quad (22.5.3.6)$$

$$= \frac{e}{\sqrt{2}} \frac{2^8 a_0}{3^5 Z} = \frac{e a_0}{Z} \frac{2^8}{\sqrt{2} 3^5} = 0.7499 \frac{e a_0}{Z} \quad (22.5.3.7)$$

b. Examine the symmetry of the integrands for  $\langle 2p_z | e x | 1s \rangle$  and  $\langle 2p_z | e y | 1s \rangle$ .

Function	Symmetry
$2p_z$	- 1
x	+ 1
1s	+ 1
y	+ 1

Under this operation the integrand of  $\langle 2p_z | e x | 1s \rangle$  is  $(-1)(1)(1) = -1$  (it is antisymmetric) and hence  $\langle 2p_z | e x | 1s \rangle = 0$ .

Similarly, under this operation the integrand of  $\langle 2p_z | e y | 1s \rangle$  is  $(-1)(1)(1) = -1$  (it is antisymmetric) and hence  $\langle 2p_z | e y | 1s \rangle = 0$ .

c.

$$\tau_R = \frac{3\hbar^4 c^3}{4 \left( \frac{3}{8} \left( \frac{e^2}{a_0} \right) Z^2 \right)^3 \left( \left( \frac{e a_0}{Z} \right) \frac{2^8}{\sqrt{2} 3^5} \right)^2}, \quad (22.5.3.8)$$

$$= \frac{3\hbar^4 c^3}{4 \frac{3^3}{8^3} \left( \frac{e^6}{a_0^3} \right) Z^6 \left( \frac{e^2 a_0^2}{Z^2} \right) \frac{2^{16}}{(2)^3 10}} \quad (22.5.3.9)$$

$$= \frac{\hbar^4 c^3 3^8 a_0}{e^8 Z^4 2^8} \quad (22.5.3.10)$$

$$\text{Inserting } e^2 = \frac{\hbar^2}{m_e a_0} \text{ we obtain :} \quad (22.5.3.11)$$

$$\tau_R = \frac{\hbar^4 c^3 3^8 a_0 m_e^4 a_0^4}{\hbar^8 Z^4 2^8} = \frac{3^8 c^3 a_0^5 m_e^4}{2^8 \hbar^4 Z^4} \quad (22.5.3.12)$$

$$= 25.6289 \frac{c^3 a_0^5 m_e^4}{\hbar^4 Z^4} \quad (22.5.3.13)$$

$$= 256,289 \left( \frac{1}{Z^4} \right) x \frac{(2.998 \times 10^{10} \text{ cm sec}^{-1})^3 (0.529177 \times 10^{-8} \text{ cm})^5 (9.109 \times 10^{-28} \text{ g})^4}{(1.0546 \times 10^{-27} \text{ g cm}^2 \text{ sec}^{-1})^4} \quad (22.5.3.14)$$

$$= 1.595 \times 10^{-9} \text{ sec } x \left( \frac{1}{Z^4} \right) \quad (22.5.3.15)$$

So, for example:

Atom	$\tau_R$
H	1.595 ns
He <sup>+</sup>	99.7 ps
Li <sup>+2</sup>	19.7 ps
Be <sup>+3</sup>	6.23 ps
Ne <sup>+9</sup>	159 fs

## Q2

a.  $H = H_0 + \lambda H'(t)$ ,  $H'(t) = V\theta(t)$ ,  $H_0\varphi_k = E_k\varphi_k$ ,  $\omega_k = \frac{E_k}{\hbar}$ ,  $i\hbar\frac{\partial\psi}{\partial t} = H\psi$

let  $\psi(r, t) = i\hbar \sum_j c_j(t) \varphi_j e^{-i\omega_j t}$  and insert into the above expression:

$$i\hbar \sum_j [\dot{c}_j - i\omega_j c_j] e^{-i\omega_j t} \varphi_j = i\hbar \sum_j c_j(t) e^{-i\omega_j t} (H_0 + \lambda H'(t)) \varphi_j \quad (22.5.3.16)$$

$$\sum_j [i\hbar \dot{c}_j + E_j c_j - c_j E_j - c_j \lambda H'] e^{-i\omega_j t} \varphi_j = 0 \quad (22.5.3.17)$$

$$\sum_j [i\hbar \dot{c}_j \langle m | j \rangle - c_j \lambda \langle m | H' | j \rangle] e^{-i\omega_j t} = 0 \quad (22.5.3.18)$$

$$i\hbar \dot{c}_m e^{-i\omega_m t} = \sum_j c_j \lambda H'_{mj} e^{-i\omega_j t} \quad (22.5.3.19)$$

So, 
$$\quad (22.5.3.20)$$

$$\dot{c}_m = \frac{1}{i\hbar} \sum_j c_j \lambda H'_{mj} e^{-i(\omega_j - \omega_m)t} \quad (22.5.3.21)$$

Going back a few equations and multiplying from the left by  $\varphi_k$  instead of  $\varphi_m$  we obtain:

$$\sum_j [i\hbar \dot{c}_j \langle k | j \rangle - c_j \lambda \langle k | H' | j \rangle] e^{-i\omega_j t} = 0 \quad (22.5.3.22)$$

$$i\hbar \dot{c}_k e^{-i\omega_k t} = \sum_j c_j \lambda H'_{kj} e^{-i\omega_j t} \quad (22.5.3.23)$$

So, 
$$\quad (22.5.3.24)$$

$$\dot{c}_k = \frac{1}{i\hbar} \sum_j c_j \lambda H'_{kj} e^{-i\omega_j t} \quad (22.5.3.25)$$

Now, let: 
$$\quad (22.5.3.26)$$

$$c_m = c_m^{(0)} + c_m^{(1)} \lambda + c_m^{(2)} \lambda^2 + \dots \quad (22.5.3.27)$$

$$c_k = c_k^{(0)} + c_k^{(1)} \lambda + c_k^{(2)} \lambda^2 + \dots \quad (22.5.3.28)$$

and substituting into above we obtain: 
$$\quad (22.5.3.29)$$

$$\dot{c}_m^{(0)} + \dot{c}_m^{(1)} \lambda + \dot{c}_m^{(2)} \lambda^2 + \dots = \frac{1}{i\hbar} \sum_j [c_j^{(0)} + c_j^{(1)} \lambda + c_j^{(2)} \lambda^2 + \dots] \lambda H'_{mj} e^{-i(\omega_j - \omega_m)t} \quad (22.5.3.30)$$

first order: (22.5.3.31)

$$\dot{c}_m^{(0)} = 0 \Rightarrow c_m^{(0)} = 1 \quad (22.5.3.32)$$

second order:  $\dot{c}_m^{(1)} = \frac{1}{i\hbar} \sum_j c_j^{(0)} H'_{mj} e^{-i(\omega_{jm})t}$  (22.5.3.33)

$(n+1)^{st}$  order: (22.5.3.34)

$$\dot{c}_m^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{mj} e^{-i(\omega_{jm})t} \quad (22.5.3.35)$$

Similarly: (22.5.3.36)

first order: (22.5.3.37)

$$\dot{c}_k^{(0)} = 0 \Rightarrow c_{k \neq m}^{(0)} = 0 \quad (22.5.3.38)$$

second order: (22.5.3.39)

$$\dot{c}_k^{(1)} = \frac{1}{i\hbar} \sum_j c_j^{(0)} H'_{kj} e^{-i(\omega_{jk})t} \quad (22.5.3.40)$$

$(n+1)^{st}$  order: (22.5.3.41)

$$\dot{c}_k^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{kj} e^{-i(\omega_{jk})t} \quad (22.5.3.42)$$

So, (22.5.3.43)

$$\dot{c}_m^{(1)} = \frac{1}{i\hbar} c_m^{(0)} H'_{mm} e^{-i(\omega_{mm})t} = \frac{1}{i\hbar} H'_{mm} \quad (22.5.3.44)$$

$$c_m^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' V_{mm} = \frac{V_{mm} t}{i\hbar} \quad (22.5.3.45)$$

and similarly, (22.5.3.46)

$$\dot{c}_k^{(1)} = \frac{1}{i\hbar} c_m^{(0)} H'_{km} e^{-i(\omega_{mk})t} = \frac{1}{i\hbar} H'_{km} e^{-i(\omega_{mk})t} \quad (22.5.3.47)$$

$$c_k^{(1)}(t) = \frac{1}{i\hbar} V_{km} \int_0^t dt' e^{-i(\omega_{mk})t'} = \frac{V_{km}}{\hbar\omega_{mk}} [e^{-i(\omega_{mk})t} - 1] \quad (22.5.3.48)$$

$$\dot{c}_m^{(2)} = \frac{1}{i\hbar} \sum_j c_j^{(1)} H'_{mj} e^{-i(\omega_{jm})t} \quad (22.5.3.49)$$

$$\dot{c}_m^{(2)} = \sum_{j \neq m} \frac{1}{i\hbar} \frac{V_{jm}}{\hbar\omega_{mj}} [e^{-i(\omega_{mj})t} - 1] H'_{mj} e^{-i(\omega_{jm})t} + \frac{1}{i\hbar} \frac{V_{mm} t}{i\hbar} H'_{mm} \quad (22.5.3.50)$$

$$c_m^{(2)} = \sum_{j \neq m} \frac{1}{i\hbar} \frac{V_{jm} V_{mj}}{\hbar\omega_{mj}} \int_0^t dt' e^{-i(\omega_{jm})t'} [e^{-i(\omega_{mj})t'} - 1] - \frac{V_{mm} V_{mm}}{\hbar^2} \int_0^t t' dt' \quad (22.5.3.51)$$

$$= \sum_{j \neq m} \frac{V_{jm} V_{mj}}{i\hbar^2 \omega_{mj}} \int_0^t dt' [1 - e^{-i(\omega_{jm})t'}] - \frac{|V_{mm}|^2}{\hbar^2} \frac{t^2}{2} \quad (22.5.3.52)$$

$$= \sum_{j \neq m} \frac{V_{jm} V_{mj}}{i\hbar^2 \omega_{mj}} \left( t - \frac{e^{-i(\omega_{jm})t} - 1}{-i\omega_{jm}} \right) - \frac{|V_{mm}|^2}{\hbar^2} \frac{t^2}{2} \quad (22.5.3.53)$$

$$= \sum_{j \neq m} \frac{V_{jm} V_{mj}}{\hbar^2 \omega_{mj}^2} (e^{-i(\omega_{jm})t} - 1) + \sum_{j \neq m} \frac{V_{jm} V_{mj}}{i\hbar^2 \omega_{mj}} t - \frac{|V_{mm}|^2 t^2}{2\hbar^2} \quad (22.5.3.54)$$

Similarly, (22.5.3.55)

$$\dot{c}_k^{(2)} = \frac{1}{i\hbar} \sum_j c_j^{(1)} H'_{kj} e^{-i(\omega_{jk})t} \quad (22.5.3.56)$$

$$= \sum_{j \neq m} \frac{1}{i\hbar} \frac{V_{jm}}{\hbar\omega_{mj}} [e^{-i(\omega_{mj})t} - 1] H'_{kj} e^{-i(\omega_{jk})t} + \frac{1}{i\hbar} \frac{V_{mm} t}{i\hbar} H'_{km} e^{-i(\omega_{mk})t} \quad (22.5.3.57)$$

$$c_k^{(2)}(t) = \sum_{j \neq m} \frac{V_{jm} V_{kj}}{i\hbar^2 \omega_{mj}} \int_0^t dt' e^{-i(\omega_{jk})t'} [e^{-i(\omega_{mj})t'} - 1] - \frac{V_{mm} V_{km}}{\hbar^2} \int_0^t t' dt' e^{-i(\omega_{mk})t'} \quad (22.5.3.58)$$

$$= \sum_{j \neq m} \frac{V_{jm} V_{kj}}{i\hbar^2 \omega_{mj}} \left( \frac{e^{-i(\omega_{mj} + \omega_{jk})t} - 1}{-i\omega_{mk}} - \frac{e^{-i(\omega_{jk})t} - 1}{-i\omega_{jk}} \right) - \frac{V_{mm} V_{km}}{\hbar^2} \left[ e^{-i(\omega_{mk})t} \left( \frac{t'}{-i\omega_{mk}} - \frac{1}{-(i\omega_{mk})^2} \right) \right]_0^t \quad (22.5.3.59)$$

$$= \sum_{j \neq m} \frac{V_{jm} V_{kj}}{\hbar^2 \omega_{mj}} \left( \frac{e^{-i(\omega_{mk})t} - 1}{\omega_{mk}} - \frac{e^{-i(\omega_{jk})t} - 1}{\omega_{jk}} \right) + \frac{V_{mm} V_{km}}{\hbar^2 \omega_{mk}} \left[ e^{-i(\omega_{mk})t} \left( \frac{t'}{i} - \frac{1}{\omega_{mk}} \right) \right]_0^t \quad (22.5.3.60)$$

$$= \sum_{j \neq m} \frac{V_{jm} V_{kj}}{E_m - E_j} \left( \frac{e^{-i(\omega_{mk})t} - 1}{E_m - E_k} - \frac{e^{-i(\omega_{jk})t} - 1}{E_j - E_k} \right) + \frac{V_{mm} V_{km}}{\hbar(E_m - E_k)} \left[ e^{-i(\omega_{mk})t} \left( \frac{t}{i} - \frac{1}{\omega_{mk}} \right) + \frac{1}{\omega_{mk}} \right] \quad (22.5.3.61)$$

So, the overall amplitudes  $c_m$ , and  $c_k$ , to second order are:

$$c_m(t) = 1 + \frac{V_{mm}t}{i\hbar} + \sum_{j \neq m}' \frac{V_{jm}V_{mj}}{i\hbar(E_m - E_j)}t + \sum_{j \neq m}' \frac{V_{jm}V_{mj}}{\hbar^2(E_m - E_j)^2}(e^{-i(\omega_{mk})t} - 1) - \frac{|V_{mm}|^2 t^2}{2\hbar^2} \quad (22.5.3.62)$$

$$c_k(t) = \frac{V_{km}}{(E_m - E_k)}[e^{-i(\omega_{mk})t} - 1] + \frac{V_{mm}V_{km}}{(E_m - E_k)^2}[1 - e^{-i(\omega_{mk})t}] + \frac{V_{mm}V_{km}}{(E_m - E_k)}\frac{t}{\hbar i}e^{-i(\omega_{mk})t} + \sum_{j \neq m}' \frac{V_{jm}V_{kj}}{E_m - E_j} \left( \frac{e^{-i(\omega_{mk})t} - 1}{E_m - E_k} - \frac{e^{-i(\omega_{jk})t} - 1}{E_j - E_k} \right) \quad (22.5.3.63)$$

b. The perturbation equations still hold:

$$\dot{c}_m^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{mj} e^{-i(\omega_{jm})t}; \quad \dot{c}_k^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{kj} e^{-i(\omega_{jk})t} \quad (22.5.3.64)$$

$$\text{So, } c_m^{(0)} = 1 \text{ and } c_k^{(0)} = 0 \quad (22.5.3.65)$$

$$\dot{c}_m^{(1)} = \frac{1}{i\hbar} H'_{mm} \quad (22.5.3.66)$$

$$c_m^{(1)} = \frac{1}{i\hbar} V_{mm} \int_{-\infty}^t dt' e^{-i(\omega)t'} = \frac{V_{mm}}{i\hbar(-i\omega_{mk} + \eta)} [e^{-i(\omega_{mk} + \eta)t}] \quad (22.5.3.67)$$

$$= \frac{V_{mm}}{E_m - E_k + i\hbar\eta} [e^{-i(\omega_{mk} + \eta)t}] \quad (22.5.3.68)$$

$$\dot{c}_m^{(2)} = \sum_{j \neq m}' \frac{1}{i\hbar} \frac{V_{jm}}{E_m - E_j + i\hbar\eta} e^{-i(\omega_{mj} + \eta)t} V_{mj} e^{\eta t} e^{-i(\omega_{jm})t} + \frac{1}{i\hbar} \frac{V_{mm} e^{\eta t}}{i\hbar\eta} V_{mm} e^{\eta t} \quad (22.5.3.69)$$

$$c_m^{(2)} = \sum_{j \neq m}' \frac{1}{i\hbar} \frac{V_{jm}V_{mj}}{E_m - E_j + i\hbar\eta} \int_{-\infty}^t e^{2\eta t'} dt' - \frac{|V_{mm}|^2}{2\hbar^2 \eta^2} \int_{-\infty}^t e^{2\eta t'} dt' = \sum_{j \neq m}' \frac{V_{jm}V_{mj}}{i\hbar 2\eta(E_m - E_j + i\hbar\eta)} e^{2\eta t} - \frac{|V_{mm}|^2}{2\hbar^2 \eta^2} e^{2\eta t} \quad (22.5.3.70)$$

$$\dot{c}_k^{(2)} = \sum_{j \neq m}' \frac{1}{i\hbar} \frac{V_{jm}}{E_m - E_j + i\hbar\eta} e^{-i(\omega_{mj} + \eta)t} H'_{kj} e^{-i(\omega_{jk})t} \quad (22.5.3.71)$$

c. In part a. the  $c^{(2)}(t)$  grow linearly with time (for  $V_{mm} = 0$ ) while in part b. they remain finite for  $\eta > 0$ . The result in part a. is due to the sudden turning on of the field.  
d.

$$|c_k(t)|^2 = \left| \sum_j \frac{V_{jm}V_{kj} e^{-i(\omega_{mk} + 2\eta)t}}{(E_m - E_j + i\hbar\eta)(E_m - E_k + 2i\hbar\eta)} \right|^2 \quad (22.5.3.72)$$

$$= \sum_{j,j'} \frac{V_{kj}V_{k'j'}V_{jm}V_{j'm} e^{4\eta t}}{[(E_m - E_j)(E_m - E_{j'}) + i\hbar\eta(E_j - E_{j'}) + \hbar^2\eta^2][(E_m - E_k)^2 + 4\hbar^2\eta^2]} \quad (22.5.3.73)$$

$$\text{Now, look at the limit as } \eta \rightarrow 0^+: \quad (22.5.3.74)$$

$$\frac{d}{dt} |c_k(t)|^2 \neq 0 \text{ when } E_m = E_k \quad (22.5.3.75)$$

$$\lim_{\eta \rightarrow 0^+} \frac{4\eta}{((E_m - E_k)^2 + 4\hbar^2\eta^2)} \alpha \delta(E_m - E_k) \quad (22.5.3.76)$$

$$\text{So, the final result is the } 2^{nd} \text{ order golden rule expression:} \quad (22.5.3.77)$$

$$\frac{d}{dt} |c_k(t)|^2 = \frac{2\pi}{\hbar} \delta(E_m - E_k) \lim_{\eta \rightarrow 0^+} \left| \frac{V_{jm}V_{kj}}{(E_j - E_m - i\hbar\eta)} \right|^2 \quad (22.5.3.78)$$

### Q3

For the sudden perturbation case:

$$|c_m(t)|^2 = 1 + \sum_j' \frac{V_{jm}V_{mj}}{(E_m - E_j)^2} [e^{-i(\omega_{jm})t} - 1 + e^{i(\omega_{jm})t} - 1] + O(V^3) \quad (22.5.3.79)$$

$$|c_m(t)|^2 = 1 + \sum_j' \frac{V_{jm}V_{mj}}{(E_m - E_j)^2} [e^{-i(\omega_{jm})t} + e^{i(\omega_{jm})t} - 2] + O(V^3) \quad (22.5.3.80)$$

$$|c_k(t)|^2 = \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [-e^{-i(\omega_{mk})t} - e^{i(\omega_{mk})t} + 2] + O(V^3) \quad (22.5.3.81)$$

$$1 - \sum_{k \neq m}' |c_k(t)|^2 = 1 - \sum_k' \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [-e^{-i(\omega_{mk})t} - e^{i(\omega_{mk})t} + 2] + O(V^3) \quad (22.5.3.82)$$

$$= 1 + \sum_k' \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [e^{-i(\omega_{mk})t} + e^{i(\omega_{mk})t} - 2] + O(V^3) \quad (22.5.3.83)$$

$\therefore$  to order  $V^2$ ,  $|c_m(t)|^2 = 1 - \sum_k' |c_k(t)|^2$ , with no assumptions made regarding  $V_{mm}$ .

For the adiabatic perturbation case:

$$|c_m(t)|^2 = 1 + \sum_{j \neq m}' \left[ \frac{V_{jm} V_{mj} e^{2\eta t}}{i\hbar 2\eta (E_m - E_j + i\hbar\eta)} + \frac{V_{jm} V_{mj} e^{2\eta t}}{-i\hbar 2\eta (E_m - E_j - i\hbar\eta)} \right] + O(V^3) \quad (22.5.3.84)$$

$$= 1 + \sum_{j \neq m}' \frac{1}{i\hbar 2\eta} \left[ \frac{1}{(E_m - E_j + i\hbar\eta)} - \frac{1}{(E_m - E_j - i\hbar\eta)} \right] V_{jm} V_{mj} e^{2\eta t} + O(V^3) \quad (22.5.3.85)$$

$$= 1 + \sum_{j \neq m}' \frac{1}{i\hbar 2\eta} \left[ \frac{-2i\hbar\eta}{(E_m - E_j)^2 + \hbar^2\eta^2} \right] V_{jm} V_{mj} e^{2\eta t} + O(V^3) \quad (22.5.3.86)$$

$$= 1 - \sum_{j \neq m}' \left[ \frac{V_{jm} V_{mj} e^{2\eta t}}{(E_m - E_j)^2 + \hbar^2\eta^2} \right] + O(V^3) \quad (22.5.3.87)$$

$$|c_k(t)|^2 = \frac{V_{km} V_{mk}}{(E_m - E_k)^2 + \hbar^2\eta^2} e^{2\eta t} + O(V^3) \quad (22.5.3.88)$$

$\therefore$  to order  $V^2$ ,  $|c_m(t)|^2 = 1 - \sum_k' |c_k(t)|^2$ , with no assumptions made regarding  $V_{mm}$  for this case as well.

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