# Errata and Addenda 

Elements of Quantum Mechanics<br>Michael D. Fayer<br>Oxford University Press

If you find errors in the book, please email them to fayer@stanford.edu.
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## Chapter 1

## Chapter 2

1. Page 7, equation 2.2.

A subscript $i$ on the $L$ is missing. The equation should read

$$
|S\rangle=\sum_{i} C_{i}\left|L_{i}\right\rangle
$$

## Chapter 3

1. Page 27, second equation.

An $i$ is missing. The equation should read

$$
e^{i k\left(x-x_{0}\right)}=\cos k\left(x-x_{0}\right)+i \sin k\left(x-x_{0}\right)
$$

2. Page 28, equation 3.26 .

The term $\sqrt{2 \pi \Delta k}$ should be $\sqrt{2 \pi} \Delta k$.
3. Page 31, equation 3.37

A parenthesis is in the wrong place. The equation should read

$$
\Psi_{\Delta k}(x, t)=\int_{-\infty}^{\infty} f(k) \exp \left[i\left(k\left(x-x_{0}\right)-\omega(k) t\right)\right] d k
$$

## Chapter 4

1. Page 36 , first line under the set of equations at the top of the page. It should read, "Applying the product rule," not the chain rule.
2. Page 40 , the line immediately following equation 4.24 should read, " $\left|c_{i}\right|^{2}$, the absolute value squared of the coefficient $c_{i}$ "
3. Page 42 , the line immediately above equation 4.29 should read,
"...consider the operator $\underline{D}$,"
not "consider the Hermitian operator $\underline{D}$,"

## Chapter 5

1. Page 56 , Figure 5.4 as drawn is actually decamethylanthracene. The ten lines from the rings should either have been omitted or had H's on their ends.

## Chapter 6

1. Page 70, equation 6.20

Powers of $\gamma$ are wrong in the second line of the equation. The second line of the equation should read

$$
-2 a_{1} \gamma-4 a_{2} \gamma^{2}-6 a_{3} \gamma^{3}-\cdots
$$

2. Page 77 , equation 6.39

The lower limit of integration is incorrect. It should be $-\infty$ rather than $\infty$.
3. Page 78, equation 6.51 .

In the middle expression, the $d \gamma$ should not be in the exponent. It is the differential operator for the integral.
4. Page 83 , forth line.

I should read, "equation (6.63c), is used," not 6.63a.
5. Page 85 , the very last line on the page should read as follows.

Adding $\underline{a}^{+}$to $\underline{a}$ and rearranging give the position operator:
6. Page 86 , last equation on page

The last line of the last equation has a raising operator instead of a lowering operator in the second bracket. The last line of the equation should read

$$
+\langle n| \underline{a}|m\rangle\langle m| \underline{a}|n\rangle+\langle n| \underline{a}^{+}|m\rangle\langle m| \underline{a}|n\rangle .
$$

The sentences on the top of page 87 should read
The second and third terms in the last equation are zero. Consider the right-hand bracket of the second term. $\underline{\mathrm{a}}^{+}$operating on $|\mathrm{n}\rangle$ gives $|\mathrm{n}+1\rangle$. For this bracket to be non-zero, $\langle\mathrm{m}|$ must be $\langle\mathrm{n}+1|$. Then for the left hand bracket of this pair, $\underline{\mathrm{a}}^{+}$operating on $|\mathrm{m}\rangle=|\mathrm{n}+1\rangle$ gives $|\mathrm{n}+2\rangle$. Closing this bracket with $\langle\mathrm{n}|$ gives zero by orthogonality of the eigenkets of the harmonic oscillator. In a similar manner, the third term is also zero.

The first and last terms are products of brackets times their complex conjugates and can be written as the absolute value squared. Therefore,
7. Page 88 , the third line of the equation should read

$$
=\sqrt{n}(\langle n \mid n-1\rangle+\sqrt{n+1}\langle n \mid n+1\rangle)
$$

## Chapter 7

1. Page 94 , bottom of page.

The line should read: "...into the Schrödinger...".
2. Page 96, equations 7.13 and 7.14 .

The numerators in the final left hand side term contain the factor " $8 \pi^{2}$ ", this should instead be " 2 ".
3. Page 98 , the paragraph containing equations 7.21 should read as follows.

The complex solutions having the same absolute values of $\mathrm{m},|\mathrm{m}|$, can be added and subtracted to give real solutions because the solutions with the same $|\mathrm{m}|$ satisfy the same differential equation. Then, any superposition of them will also satisfy the differential equation. Then the solutions to equation 7.15 are also

$$
\begin{array}{ll}
\Phi_{0}(\varphi)=\frac{1}{\sqrt{2 \pi}} & \mathrm{~m}=0 \\
\Phi_{|\mathrm{m}|}(\varphi)=\frac{1}{\sqrt{\pi}} \cos |\mathrm{~m}| \varphi & \\
\Phi_{|\mathrm{m}|}(\varphi)=\frac{1}{\sqrt{\pi}} \sin |\mathrm{~m}| \varphi & |\mathrm{m}|=1, \tag{7.21b}
\end{array}
$$

The expression with cos is used for positive values of m , and the expression with sin is used for negative values of m .
4. Page 102, last line of the first paragraph.

The line should read "...using the product rule...", not "...using the chain rule...".
5. Page 105, fifth line of the paragraph below equation 7.52a.
"descimal" should read "decimal".
6. Page $108-109$, In all of the equations 7.63 though 7.67 , the variable is $\rho$. In equation 7.64 a , the equation below 7.64 b . and the equation below 7.65 , typographical errors have substituted the Roman alphabet letter $p$ for the Greek alphabet letter $\rho$.
7. Page 110, equation 7.70 is not normalized because it does not include the integral over angles. The equation gives the correct unnormalized radial distribution, which shows the relative probability of finding an electron in a thin spherical shell a distance $r$ from the
nucleus. Note that the normalization constant for $R_{n l}(r)$ contains a $1 / \sqrt{a_{0}^{3}}$, which when squared has units one over length cubed, canceling the units in the $r^{2} d r$, so the radial distribution function is unitless.

## Chapter 8

1. Page 128, equation 8.49 .

The sum on the right hand side should begin with $M_{0}$ not $M_{1}$.
2. Page 128 , the line below equation 8.49 .

The line should read, "...the $j^{\text {th }}$ molecule is excited, ..."

## Chapter 9

1. Pages 134 and 135, equations 9.8 and 9.11 .

The $\underline{H}$ in each of the equations should read $\underline{H}^{\prime \prime}$.
2. Page 144, equations 9.54 and 9.56 .

The summations on the right hand sides of equations 9.54 and 9.56 summations should be over n for both the numerator and the denominator. The summation symbols were incorrectly made to small and placed in the numerator. They should be larger and encompass both the numerator and denominator as in the first sum after the first equal sign in equation 9.54. The sums should also be primed indicating that the sums are for n $\neq \mathrm{m}$.
3. Page 148, the second line of equation 9.77.

The first term should read $H_{21}^{\prime} c_{1}$
4. Page 150 , equations $9.84-9.86$ and the following unnumbered equation

All of the energies in the denominators of the various terms in these equations should have superscripts, 0 (zero). These are the zeroth order energies of the states.

## Chapter 10

1. Page 159 , equation 10.35 .

The summation should be over $j$ not $i$.

## Chapter 11

1. The following is an addition to Chapter 11. It should be read at the end of Chapter 11. Fermi's Golden Rule - an important result from time dependent perturbation theory

Fermi's Golden Rule describes the relaxation of an initially prepared state into a dense manifold states to which the initial state is weakly coupled. For example, electronic excitation from the ground electronic state, $\mathrm{S}_{0}$, of a large molecule, to the first electronic
 excited state can be followed by radiationless relaxation back to the ground electronic state. This occurs because the initially excited state, $S_{1}$, is coupled to the dense manifold of vibrational states of the ground electronic state. For a molecule such as anthracene, with its first electronic transition at $\sim 25,000 \mathrm{~cm}^{-1}$, the density of ground vibrational states is extremely high, typically in the range of $10^{12}$ to $10^{18}$ states $/ \mathrm{cm}^{-1}$. The $\mathrm{S}_{1}$ excited state will relax into manifold of highly excited ground vibrational states. This is called internal conversion. In condensed phase systems, subsequent vibrational relaxation and energy flow into the solvent turns the electronic excitation into heat. Radiationless relaxation competes with fluorescent emission, and reduces the quantum yield of fluorescence. The extent of fluorescent emission depends on the competition between fluorescence and internal conversion.

To determine the rate of relaxation of relaxation of an initially prepared state into a dense manifold of state, first consider a pair of states separated in energy by $\Delta E=E_{f}-E_{i}$, where $f=$ final and $i=$ initial. The initial and final state are:
$\left|I^{0}(q, t)\right\rangle$ and $\left|F^{0}(q, t)\right\rangle$, where these are states of the time independent Hamiltonian, $\underline{H}^{0}$ , in which the states are not coupled. $q$ represents spatial coordinates, and $t$ is time. Then from time dependent perturbation theory (equation 11.11),
$\dot{C}_{F}=-\frac{i}{\hbar}\left\langle F^{0}(q, t)\right| \underline{H^{\prime}}\left|I^{0}(q, t)\right\rangle$.
The time dependence is express through

$$
\begin{array}{ll}
\left\langle F^{0}(q, t)\right| \underline{H}\left|I^{0}(q, t)\right\rangle=0 & t<0 \\
\left\langle F^{0}(q, t)\right| \underline{H}\left|I^{0}(q, t)\right\rangle=e^{i E_{f} t / \hbar}\left\langle f^{0}(q)\right| \underline{H^{\prime}}\left|i^{0}(q)\right\rangle e^{-i E_{t} t / \hbar}=e^{i\left(E_{f}-E_{i}\right) t / \hbar} H_{f i}^{\prime}=e^{i\left(E_{f}-E_{i}\right) t / \hbar} z & t \geq 0 .
\end{array}
$$

$\underline{H}^{\prime}$ only operates on the spatial part of the state vectors, so the time dependent phase factors can be taken out of the bracket. The kets $\left|i^{0}(q)\right\rangle$ and $\left|f^{0}(q)\right\rangle$ are the time independent parts of the kets. In the electronic excitation problem $t=0$ is the time at which the molecule is excited.

With $\Delta E=E_{f}-E_{i}$,

$$
\begin{aligned}
C_{F} & =-\frac{i z}{\hbar} \int_{0}^{t} e^{i \Delta E t / \hbar} d t \\
& =-\frac{i z}{\hbar} \int_{0}^{t}\left[\cos \frac{\Delta E}{\hbar} t+i \sin \frac{\Delta E}{\hbar} t\right] d t \\
& =-\left.\frac{i z}{\hbar}\left[\frac{\hbar}{\Delta E} \sin \frac{\Delta E}{\hbar} t-i \frac{\hbar}{\Delta E} \cos \frac{\Delta E}{\hbar} t\right]\right|_{0} ^{t} \\
& =-\frac{i z}{\Delta E}\left[\sin \frac{\Delta E}{\hbar} t-i \cos \frac{\Delta E}{\hbar} t+i\right]
\end{aligned}
$$

Then the probability of finding the system in the final state is
$C_{F} C_{F}^{*}=\frac{2 z^{2}}{\Delta E^{2}}\left[1-\cos \frac{\Delta E}{\hbar} t\right]$.
Using
$1-\cos x=2 \sin ^{2}(x / 2)$
$C_{F} C_{F}^{*}=\frac{4 z^{2}}{\Delta E^{2}} \sin ^{2}\left(\frac{\Delta E}{2 \hbar} t\right)$

The probability, $C_{F} C_{F}^{*}$, must be small to use time dependent perturbation theory. At very short time, the argument of $\sin ^{2}$ is small, and $\sin ^{2}(x)=x^{2}$ for small $x$, so

$$
\frac{4 z^{2}}{\Delta E^{2}} \sin ^{2}\left(\frac{\Delta E}{2 \hbar} t\right)=\frac{|z|^{2} t^{2}}{\hbar^{2}}
$$

The exact solution from the time dependent two state problem in Chapter 8 (Equation $8.40 b$ ) is

$$
C_{F} C_{F}^{*}=\frac{2 z^{2}}{\Delta E^{2}+4 z^{2}}\left(1-\cos \frac{\sqrt{\Delta E^{2}+4 z^{2}}}{\hbar} t\right) .
$$

Expanding the exact solution for short time using
$\cos x=1-\frac{x^{2}}{2!}+\cdots$
gives

$$
\begin{array}{cr} 
& 0.035 \\
\mathbf{z}=\mathbf{2 0} \mathbf{~ c m}^{-1} & 0.03 \\
\boldsymbol{t}=\mathbf{5 0} \mathbf{~ f \mathbf { s }} & 0.02 \\
\hline
\end{array}
$$

The exact solution and the time dependent perturbation theory result are identical at short time.

The time dependent perturbation theory result, $C_{F} C_{F}^{*}=\frac{4 z^{2}}{\Delta E^{2}} \sin ^{2}\left(\frac{\Delta E}{2 \hbar} t\right)$, is the square of a zeroth order spherical Bessel function. The figure shows a plot for a particular set of parameters, $z=20 \mathrm{~cm}^{-1}$ and $t=50 \mathrm{fs}$.

This is a plot of the final probability at a single time with $z$ and $t$ picked to keep the final maximum probability relatively low ( $3.5 \%$ ) as required to use time dependent perturbation theory.

To this point, the derivation is for the initial state coupled to a single final state. As discussed at the beginning, the problem is the initial state coupled to a dense manifold of final states. To proceed, the reasonable assumptions are made.

1. Most of the transition probability is close to $\Delta E=0$. Therefore, take the density of state, $\rho$, which is a function of energy to be constant with the value at $\Delta E=0$.
2. The coupling bracket $\left\langle f^{0}(q)\right| \underline{H}\left|i^{0}(q)\right\rangle=H_{f i}^{\prime}=z$ can vary with $f$ through the manifold of final states. Take them all to be equal to $z$, which is now some average value for the final state coupling to the initial state.

Then, the transition probability of being in the manifold of final states is
$P_{\text {fman }}=4 z^{2} \rho \int_{-\infty}^{\infty} \frac{\sin ^{2}\left(\frac{\Delta E t}{2 \hbar}\right)}{\Delta E^{2}} d \Delta E$.
Let
$x=\frac{\Delta E t}{2 \hbar}$ and $d x=\frac{t}{2 \hbar} d \Delta E$,
then
$P_{\text {fman }}=\frac{2 z^{2} \rho t}{\hbar} \int_{-\infty}^{\infty} \frac{\sin ^{2} x}{x^{2}} d x$.
Using

$$
\begin{aligned}
& \int_{-\infty}^{\infty} \frac{\sin ^{2} x}{x^{2}} d x=\pi, \\
& P_{\text {fman }}=\frac{2 \pi z^{2} \rho t}{\hbar} \\
& \left.P_{\text {fman }}=\frac{2 \pi \rho}{\hbar}\left|\left\langle f^{0}(q)\right| \underline{H^{\prime}}\right| i^{0}(q)\right\rangle\left.\right|^{2} t
\end{aligned}
$$

The transition probability per unit time, $k$, is
$\left.k=\frac{2 \pi}{\hbar} \rho\left|\left\langle f^{0}(q)\right| \underline{H}^{\prime}\right| i^{0}(q)\right\rangle\left.\right|^{2}$
This is Fermi's Golden Rule. It is the rate of gain of probability per unit time in the manifold of final states which is equal to the rate of loss of probability per unit time from the initial state.

The probability of being in the initial state can decay to zero without violating the approximation inherent in time dependent perturbation theory because there are so many states in the manifold of final states that none of them ever gains much probability. Therefore, coupling between states in the $f$ manifold and transfer of probability among them in negligible.

Because the loss of probability from the state $i$ per unit time is a constant,
$\frac{d P_{i}}{d t}=-k P_{i}$
and
$P_{i}=e^{-k t}$.
The probability of being in the initial state decays exponentially with the decay constant given by Fermi's Golden Rule. For an electronic excited state, the probability can also decay by fluorescence (see Chapter 12). In that case, the measured fluorescence decay constant is the sum of the spontaneous emission decay constant (equation 12.87) and the radiationless relaxation decay constant given by Fermi's Golden Rule.

## Chapter 12

1. Page 173 , equation 12.4 a

The $x$ should be a cross product, $x$.
2. Page 178 , equation 12.41 b

The $x$ in the expression following the first equal sign should be a cross product, $\times$.
3. Page 179 , equation 12.44

On the right hand side in the exponent, the factor $t / \hbar$ appears as a subscript. It should be a normal multiplicative factor of $\left(E_{m}-E_{n}\right)$.
4. Page 188 , equation 12.87

In mks units, there should be a $4 \pi \varepsilon_{0}$ in the denominator of the right hand side of the equation.

## Chapter 13

1. Page 199 , second sentence under equation 13.43

The sentence begins, "The for the...". It should read, "For the...".
2. Page 200, one set of indices in equation 13.45 on the left hand side is interchanged.

The equation should read

$$
\sum_{l} \sum_{k} u_{l j}^{*} u_{i k}\left\langle e^{l} \mid e^{k}\right\rangle=\delta_{i j}
$$

3. Page 200, one set of indices in equation 13.46 on the left hand side is interchanged. The equation should read

$$
\sum_{k} u_{k j}^{*} u_{i k}=\delta_{i j}
$$

## Chapter 14

1. Page 220 , beginning below equation 14.48 , as an addendum to see more clearly the origin of equation 14.49.

To see the form of Equation 14.48, write out $\varrho(t)$ as $|t\rangle\langle t|$

$$
\begin{equation*}
\langle t| \underline{A}|t\rangle=\sum_{i, j}\langle j \mid t\rangle\langle t \mid i\rangle\langle i| \underline{A}|j\rangle . \tag{14.48.1}
\end{equation*}
$$

Consider

$$
\begin{align*}
& \langle t \mid i\rangle\langle i| .  \tag{14.48.2}\\
& \langle t|=\sum_{k} C_{k}^{*}(t)\langle k| \tag{14.48.3}
\end{align*}
$$

Then,

$$
\begin{equation*}
\left[C_{k}^{*}(t)\langle k|\right]|i\rangle\langle i|=C_{i}^{*}(t)\langle i| . \tag{14.48.4}
\end{equation*}
$$

Performing the sum over $i$ in Equation 14.48.1,

$$
\begin{equation*}
\sum_{i} C_{i}^{*}(t)\langle i|=\langle t| . \tag{14.48.5}
\end{equation*}
$$

Then the right hand side of 14.48 .1 becomes,

$$
\begin{equation*}
\sum_{j}\langle j \mid t\rangle\langle t| \underline{A}|j\rangle=\sum_{j}\langle j| \underline{\rho}(t) \underline{A}|j\rangle, \tag{14.48.6}
\end{equation*}
$$

which is Equation 14.49.
2. Page 220, beginning with the third sentence under equation 14.50 .

The third and forth sentences should read,
"The density matrix carries the time dependence of the coefficients. In calculating the matrix elements, $A_{i j}$, time-dependent phase factors arising from the basis vectors are included as part of the matrix elements."

The forth sentence incorrectly says "not included."
3. Page 221 , immediately following equation 14.52 , a sentence should be added that reads,
"Because the states are degenerate, the product of the time dependent phase factors in the off-diagonal matrix elements of the Hamiltonian matrix yield 1."
4. Page 221, an addendum following the paragraph containing equation 14.53 .

Another property that can be calculated with the density matrix formalism is the probability of measuring a particular observable (eigenvalue) for a system that is in a superposition state. The results obtained here are necessary to clarify the discussion given in Chapter 14.G, Pure and Mixed Density Matrices.

Let $\alpha_{i}$ be the eigenvalues of the operator $\underline{A}$ having eigenvectors $\left|a_{i}\right\rangle$.

$$
\begin{equation*}
\underline{A}\left|a_{i}\right\rangle=\alpha_{i}\left|a_{i}\right\rangle \tag{14.53.1}
\end{equation*}
$$

In the complete orthonormal basis set $\{|n\rangle\}$

$$
\begin{equation*}
\left|a_{i}\right\rangle=\sum_{k} b_{k}^{i}\left|n_{k}\right\rangle, \tag{14.53.2}
\end{equation*}
$$

where the superscript $i$ on the $b_{k}^{i}$ indicates that these are the coefficients for the $i$ th eigenket of $\underline{A}$.
$\mathbb{S}\left(\alpha_{i}\right)$ is the probability of measuring $\alpha_{i}$ at time $t$ when the system is in the state

$$
\begin{equation*}
|t\rangle=\sum_{j} C_{j}(t)\left|n_{j}\right\rangle . \tag{14.53.3}
\end{equation*}
$$

The $\left|a_{i}\right\rangle$ and $|t\rangle$ are written in the same basis set $\{|n\rangle\}$. The $\mathbb{S}\left(\alpha_{i}\right)$ can be obtained using projection operators (Chapter 8.B). The projection operator is

$$
\begin{equation*}
\underline{P}_{a_{i}}=\left|a_{i}\right\rangle\left\langle a_{i}\right| . \tag{14.53.4}
\end{equation*}
$$

Then

$$
\begin{equation*}
\mathbb{S}\left(\alpha_{i}\right)=\langle t| \underline{P}_{a_{i}}|t\rangle, \tag{14.53.5}
\end{equation*}
$$

which is the expectation value of the projection operator, $\underline{P}_{a_{i}}$.
$\mathbb{S}\left(\alpha_{i}\right)$ can be calculated using the density matrix. Equation 14.50 is

$$
\langle\underline{A}\rangle=\operatorname{Tr}\{\underline{\underline{\rho}}(t) \underline{\underline{A}}\} .
$$

However, Equation 14.53 .5 states that $\mathbb{S}\left(\alpha_{i}\right)$ is the expectation value of the projection operator, $\underline{P}_{a_{i}}$. Therefore,

$$
\begin{equation*}
\mathbb{S}\left(\alpha_{i}\right)=\operatorname{Tr}\left\{\underline{\underline{\rho}}(t) \underline{\underline{P}}_{a_{i}}\right\}, \tag{14.53.6}
\end{equation*}
$$

where $\underline{\underline{\rho}}(t)$ and $\underline{\underline{\underline{P}}} a_{i}$ are written in the same basis.
As an example, consider the time dependent two state problem of Chapter 14.C. Using the basis set of Chapter 14.C,

$$
\{|1\rangle,|2\rangle\}
$$

the energy eigenkets in this basis are (see Equations 13.95 and 13.98)
with energy eigenvalues

$$
\begin{align*}
& E_{+}=E+\hbar \beta  \tag{14.53.8}\\
& E_{-}=E-\hbar \beta
\end{align*}
$$

Given that the system is in the state $|t\rangle$ of Chapter 14.C

$$
|t\rangle=C_{1}(t)|1\rangle+C_{2}(t)|2\rangle,
$$

The probability of measuring the eigenvalue, $E_{+}$is

$$
\begin{equation*}
\mathbb{S}\left(E_{+}\right)=\operatorname{Tr}\left\{\underline{\underline{\rho}}(t) \underline{\underline{P}}_{+}\right\} \tag{14.53.9}
\end{equation*}
$$

with

$$
\begin{equation*}
\underline{P}_{+}=|+\rangle\langle+| . \tag{14.53.10}
\end{equation*}
$$

The matrix $\underline{\underline{P}}_{+}$is

$$
\underline{\underline{P}}_{+}=\begin{gather*}
|1\rangle \\
|2\rangle  \tag{14.53.11}\\
\langle 1|\left(\begin{array}{ll}
1 / 2 & 1 / 2 \\
1 / 2 & 1 / 2
\end{array}\right) .
\end{gather*}
$$

For example,

$$
\begin{align*}
\langle 1 \mid+\rangle\langle+\mid 1\rangle & =\langle 1|\left[\frac{1}{\sqrt{2}}|1\rangle+\frac{1}{\sqrt{2}}|2\rangle\right] \cdot[\text { C. C. }]  \tag{14.53.12}\\
& =\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}}=\frac{1}{2},
\end{align*}
$$

where [C. C.] stands for the complex conjugate of the preceding term.
The density matrix is

$$
\underline{\underline{\rho}}(t)=\left(\begin{array}{ll}
\rho_{11} & \rho_{12}  \tag{14.53.13}\\
\rho_{21} & \rho_{22}
\end{array}\right)
$$

where $\rho_{11}, \rho_{22}, \rho_{12}$, and $\rho_{21}$ are given by Equations $14.38,14.39,14.42$, and 14.43.
Using Equations 14.53 .11 and 14.53.13 in Equation 14.53 .9 gives

$$
\begin{align*}
\mathbb{S}\left(E_{+}\right) & =\operatorname{Tr}\left\{\left(\begin{array}{ll}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{array}\right)\left(\begin{array}{ll}
1 / 2 & 1 / 2 \\
1 / 2 & 1 / 2
\end{array}\right)\right\} \\
& =\frac{1}{2}\left[\rho_{11}+\rho_{12}+\rho_{21}+\rho_{22}\right]  \tag{14.53.14}\\
& =\frac{1}{2}\left[\cos ^{2}(\beta t)+\frac{i}{2} \sin (2 \beta t)-\frac{i}{2} \sin (2 \beta t)+\sin ^{2}(\beta t)\right] \\
& =\frac{1}{2} .
\end{align*}
$$

This is the same result (Equation 8.32a) found in Chapter 8 using the projection operator.
5. Page 222, equations $14.55,14.56$, and 14.57 .

The $\hbar$ (h bar) on the right hand sides of these equations should be deleted.
6. Page 222, equation 14.58

The right hand side should be divided by $\hbar$ (h bar). The equation should read

$$
\omega_{1}=\mu E_{0} / \hbar
$$

7. Page 225, equation 14.71 d

The left hand side should read, $\rho_{21}$
8. Page 226 , equation 14.76

The matrix should be multiplied by $\hbar$ (h bar).
9. Page 227, immediately following equation 14.80 , sentences should be added that read,
"The matrix elements of $\underline{\mu}$ involve the time independent kets $\left|1^{\prime}\right\rangle$ and $\mid 2$ ' $\rangle$ (see equations 14.56). Therefore, there are no time dependent phase factors in the matrix. This is a special case. In general, when finding the expectation value of an operator, $\underline{A}$, the kets may contain time dependent phase factors, and the off-diagonal matrix elements can have time dependent phase factors."
10. Page 228, an addendum following Equation 14.85 .

Given Equations 14.84 and 14.85 , which describe a statistical mixture of subensembles of independent systems (not to be confused with a superposition state), the probability $\mathbb{S}\left(\alpha_{i}\right)$ that a measurement of an observable represented by the operator, $\underline{A}$, will yield the value $\alpha_{i}$ can be calculated using the density matrix formalism. As in the addendum following Equation 14.53 (see above) using projection operators,

$$
\begin{equation*}
\mathbb{S}_{k}\left(\alpha_{i}\right)=\left\langle t_{k}\right| \underline{P}_{a_{i}}\left|t_{k}\right\rangle, \tag{14.85.1}
\end{equation*}
$$

where $\mathbb{S}_{k}\left(\alpha_{i}\right)$ is the probability of measuring $\alpha_{i}$ if the system is in the state $\left|t_{k}\right\rangle . \underline{P}_{a_{i}}$ is the projection operator

$$
\underline{P}_{a_{i}}=\left|a_{i}\right\rangle\left\langle a_{i}\right| .
$$

Then $\mathbb{S}\left(\alpha_{i}\right)$ is the weighted sum over the $\mathbb{S}_{k}\left(\alpha_{i}\right)$, that is,

$$
\begin{equation*}
\mathbb{S}\left(\alpha_{i}\right)=\sum_{k} P_{k} \mathbb{S}_{k}\left(\alpha_{i}\right) \tag{14.85.2}
\end{equation*}
$$

where the $P_{k}$ are defined by Equations 14.84 and 14.85 .
Using the result in the addendum following Equation 14.53 (addendum Equation 14.53.6)

$$
\begin{equation*}
\mathbb{S}_{k}\left(\alpha_{i}\right)=\operatorname{Tr}\left\{\underline{\underline{\rho}}_{k}(t) \underline{\underline{P}}_{a_{i}}\right\} \tag{14.85.3}
\end{equation*}
$$

where

$$
\begin{equation*}
\underline{\rho}_{k}=\left|t_{k}\right\rangle\left\langle t_{k}\right| . \tag{14.85.4}
\end{equation*}
$$

$\underline{\rho}_{k}$ is the density operator for state $\left|t_{k}\right\rangle$, which belongs to the $k^{\text {th }}$ subensemble.
Substituting Equation 14.85.3 into Equation 14.85 .2 gives

$$
\begin{align*}
\mathbb{S}\left(\alpha_{i}\right) & =\sum_{k} P_{k} \operatorname{Tr}\left\{\underline{\underline{\rho_{k}}}(t) \underline{\underline{P}}_{a_{i}}\right\} \\
& =\operatorname{Tr}\left\{\sum_{k} P_{k} \underline{\underline{\rho}}_{k}(t) \underline{\underline{P}}_{a_{i}}\right\}  \tag{14.85.5}\\
& =\operatorname{Tr}\left\{\underline{\underline{\rho}}(t) \underline{\underline{P_{i}}}\right\}
\end{align*}
$$

where

$$
\begin{equation*}
\underline{\underline{\rho}}(t)=\sum_{k} P_{k} \underline{\underline{\rho}}_{k}(t) . \tag{14.85.6}
\end{equation*}
$$

$\underline{\underline{\rho}}(t)$ is the average of the density matrices $\underline{\underline{\rho}}_{k}(t) . \underline{\underline{\rho}}(t)$ is the definition of the density matrix for a system that is a statistical mixture. All physical predictions can be made using $\underline{\underline{\rho}}(t)$, the average of the density matrices $\underline{\underline{\rho}}_{k}(t)$.
11. Page 230 , equation 14.94

In the second line of the equation, $\sin \delta$ should read $\sin (\delta t)$, and $\cos \delta$ should read $\cos (\delta t)$.

## Chapter 15

1. Page 253, the table of Clebsch-Gordon coefficients

In the column for $1 / 21 / 2$, the second number should be $-\sqrt{1 / 3}$, the negative sign is missing.

In the column for $1 / 2-1 / 2$, the second number should be $-\sqrt{2 / 3}$, the negative sign is missing.

## Chapter 16

1. Page 257 , equation 16.4

In equation 16.4, one Bohr magneton is given as

$$
\frac{e \hbar}{2 m c}
$$

where $m$ is the mass of the electron. As given, the formula is in Gaussian units.

$$
\frac{e \hbar}{2 m c}=9.27410 \times 10^{-21} \mathrm{erg} / \mathrm{G}
$$

where $\mathrm{G}=$ gauss.
In SI units

$$
\frac{e \hbar}{2 m}=9.27410 \times 10^{-24} \mathrm{~J} / \mathrm{T}
$$

where $\mathrm{T}=$ tesla.
2. Page 264 , equation 16.35

The bottom two bras on the left hand side of the matrix should be $\left\langle-1 \frac{1}{2}\right|$ and
$\left\langle-1-\frac{1}{2}\right|$. In addition, the vertical line that forms the right side of each of the bras should have gaps between the bras.
3. Page 269 , equation 16.48

In the second diagonal matrix element, the lower case $j_{s}$ should be upper case, $J_{s}$.

## Chapter 17

1. In Chapter 17 and in other places throughout the book, the letter $e$ is used for two purposes, the charge on the electron and the base of the natural logarithm. It is possible for these two uses to appear in the same equation. Examples are equations 17.24 and 17.34. In equation 17.34 the factor multiplying the terms in square brackets contains $e^{2}$. This is the charge on the electron. Frequently, the charge on the electron will be divided by $4 \pi \varepsilon_{0}$. The term inside the square brackets, $e^{-2 D}$, is $\operatorname{Exp}(-2 D)$. Hopefully, the context and factors of $4 \pi \varepsilon_{o}$ will make it clear which usage of $e$ is intended.
2. Page 290, equations 17.29 and 17.30

The wavefunction on the left inside each double integral formally should be the complex conjugate, $\psi_{I}^{*}$. The results are not changed because the functions are real.

## Problems

1. Page 295, Chapter 2 problems, problem 1, the first $\gamma$ in the second equation should be underlined, i.e., $\not$.
2. Page 297 , Chapter 4 problems, problem 2 b , $f$ on the right hand side of the equation should be $f(x)$.
3. Page 297, Chapter 4 problems, problem 2c, after the equation it should read, "where $n$ is any positive integer."
4. Page 299, Chapter 6 problems, problem 1, the second sentence should read Using the generating functions $S(\gamma, s) \ldots$
5. Page 300, Chapter 6 problems, problem 1, the two equations at the top of the page

In the exponential on the right hand side of the equation for $S(\gamma, s)$, the $(2-\gamma)$ should be $(s-\gamma)$.

In the equation for $T(\gamma, s)$, the sum should be over $m$ not $n$.
6. Page 309, problem 13.2

Following the second set of equations, the problem should read,
" $\gamma$ is the strength of the interaction (the off diagonal coupling matrix element).
Generally, $\mathrm{E}_{\ell}>\mathrm{E}_{\mathrm{m}}$ and $|\gamma|<\left(\mathrm{E}_{\ell}-\mathrm{E}_{\mathrm{m}}\right)$. To simplify the math in this problem, a special case is considered which obeys the above inequalities but takes $\gamma$ to be positive and uses the specific situation"
7. Page 310, problem 15.2

The problem should read, "For $j=3 / 2$, where $j$ is the maximum eigenvalue of the operator $\underline{\mathrm{J}}_{z}$, find the explicit matrices for the operators $\underline{\mathrm{J}}^{2}, \underline{\mathrm{~J}}_{z}, \underline{\mathrm{~J}}_{+}$, and $\underline{\mathrm{J}}$.."

## Physical Constants and Conversion Factors for Energy Units

1. Page 314, table of Physical Constants

The entry for $4 \pi \varepsilon_{o}$ should be $1.11265 \times 10^{-10} \mathrm{~J}^{-1} \mathrm{C}^{2} \mathrm{~m}^{-1}$.

