Chapter 1

The foundations of quantum mechanics

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Exercises

1.1 (a) \( \int (f + g) \, dx = \int f \, dx + \int g \, dx \); linear.

(b) \( (f + g)^{1/2} \neq f^{1/2} + g^{1/2} \); nonlinear.

(c) \( f(x + a) + g(x + a) = f(x + a) + g(x + a) \); linear.

(d) \( f(-x) + g(-x) = f(-x) + g(-x) \); linear.

Exercise: Repeat the exercise for (a) differentiation, (b) exponentiation.

1.2 (a) \( \frac{d}{dx} e^{ax} = ae^{ax} \); \( e^{ax} \) is an eigenfunction, eigenvalue \( a \).

\[
\frac{d}{dx} e^{ax^2} = 2axe^{ax^2}; \quad e^{ax^2} \text{ not an } \text{e.f.}
\]

\( \frac{d}{dx} x = 1; \quad x \text{ not an } \text{e.f.} \)

\( \frac{d}{dx} x^2 = 2x; \quad x^2 \text{ not an } \text{e.f.} \)

\( \frac{d}{dx} (ax + b) = a; \quad ax + b \text{ not an } \text{e.f.} \)

\( \frac{d}{dx} \sin x = \cos x; \quad \sin x \text{ not an } \text{e.f.} \)

(b) \( \frac{d^2}{dx^2} e^{ax} = a^2 e^{ax} \); \( e^{ax} \) is an eigenfunction, eigenvalue \( a^2 \).

\[
\frac{d^2}{dx^2} e^{ax^2} = 2ae^{ax^2} + 4a^2x^2e^{ax^2}; \quad e^{ax^2} \text{ not an } \text{e.f.}
\]

\( \frac{d^2}{dx^2} x = 0 = 0x; \quad x \text{ is an } \text{e.f.; e.v. is } 0. \)

\( \frac{d^2}{dx^2} x^2 = 2; \quad x^2 \text{ not an } \text{e.f.} \)

\( \frac{d^2}{dx^2} (ax + b) = 0 = 0(ax + b); \quad ax + b \text{ is an } \text{e.f.; e.v. is } 0. \)

\( \frac{d^2}{dx^2} \sin x = -\sin x; \quad \sin x \text{ is an } \text{e.f.; e.v. is } -1. \)
**Exercise:** Find the operator of which $e^{ax^2}$ is an eigenfunction. Find the eigenfunction of the operator ‘multiplication by $x^2$.

1.3

$$\langle m | A + iB | n \rangle = \langle m | A | n \rangle + i \langle m | B | n \rangle$$

$$= \langle n | A | m \rangle^* + i \langle n | B | m \rangle^* \quad [A, B \text{ hermitian}, \text{eqn 1.26}]$$

$$= \{ \langle n | A | m \rangle - i \langle n | B | m \rangle \}^* = \langle n | A - iB | m \rangle^*.$$  

Hence, $A - iB$ is the hermitian conjugate of $A + iB$ (and $A + iB$ is not self-conjugate, another term for hermitian).

**Exercise:** Confirm that $x + (d/dx)$ and $x - (d/dx)$ are hermitian conjugates.

1.4 If the maximum uncertainty in the position $x$ of the electron is $\Delta x$, the minimum uncertainty in the momentum $p_x$ will be given by $\Delta x \Delta p_x = \frac{1}{2} \hbar$. Since the electron is confined to the linear box, $\Delta x = 0.10$ nm. Therefore

$$\Delta p_x = \frac{\hbar}{2\Delta x}$$

$$= \frac{1.055 \times 10^{-34} \text{ J s}}{2 \times 0.10 \times 10^{-9} \text{ m}}$$

$$= 5.3 \times 10^{-25} \text{ kg m s}^{-1}$$

(a) Since $p_x = m_e v$, the uncertainty in the velocity is

$$\Delta v = \Delta p_x / m_e$$

$$= (5.3 \times 10^{-25} \text{ kg m s}^{-1}) / (9.109 \times 10^{-31} \text{ kg})$$

$$= 5.8 \times 10^5 \text{ m s}^{-1}$$
(b) Since, \( E_K = \frac{p_x^2}{2m_e} \)

\[
\Delta E_K = (\Delta p_x)^2/2m_e
\]

\[
= (5.3 \times 10^{-25} \text{ kg m s}^{-1})^2/(2 \times 9.10938 \times 10^{-31} \text{ kg})
\]

\[
= 1.5 \times 10^{-19} \text{ J}
\]

**Exercise:** If the length of the box is doubled to 0.20 nm, what are the minimum uncertainties? If a proton is confined to a linear box of length 0.20 nm, what are the minimum uncertainties?

1.5

Use the integral

\[
\int x^2 \sin^2 ax \, dx = \frac{1}{6} x^3 + \left(1/4a^2\right)\left(\frac{1}{2} \sin(2ax) - ax \cos(2ax) - a^2 x^2 \sin(2ax)\right)
\]

\[
\langle x^2 \rangle_n = \left(\frac{2}{L}\right) \int_0^L x^2 \sin^2 (n\pi x / L) \, dx = \frac{1}{L^2} \left\{ 1 - \left( 3/2n^2 \pi^2 \right) \right\}
\]

\[
\langle x^2 \rangle_2 = \frac{1}{L^2} \left\{ 1 - \left( 3/8 \pi^2 \right) \right\}
\]

Since the particle is equally likely to be found in the right-hand side of the box (between \( L/2 \) and \( L \)) and in the left-hand side of the box (between 0 and \( L/2 \)), the average value \( \langle x \rangle = L/2 \) for all values of \( n \). Therefore,

\[
\Delta x_n = \{\langle x^2 \rangle_n - \langle x \rangle^2\}^{1/2} = \left\{ \frac{1}{3} L^2 - \left( 1/2n^2 \pi^2 \right) L^2 - \frac{1}{4} L^2 \right\}^{1/2}
\]

\[
= \left( L / 2 \sqrt{3} \right) \left\{ 1 - \left( 6/ n^2 \pi^2 \right) \right\}^{1/2}
\]

\[
\Delta x_2 = \left( L / 2 \sqrt{3} \right) \left\{ 1 - \left( 3/2 \pi^2 \right) \right\}^{1/2}
\]

As for the momentum, the intuitive solution is \( \langle p \rangle_n = 0 \) because the wavefunction is a standing wave. The elegant solution is
\[ \langle p \rangle = \langle n|p|n \rangle = \langle n|p|n \rangle^* \text{ [hermiticity]} = \langle n|p^*|n \rangle = -\langle n|p|n \rangle \text{ [}p^* = -p\text{]}.
\]

Therefore since \( \langle p \rangle = -(\langle p \rangle) \), \( \langle p \rangle = 0 \).

The straightforward solution is:

\[
\langle p \rangle_n = (\hbar/i)(2/L) \int_0^L \sin(n\pi x / L)(d / dx) \sin(n\pi x / L) dx
\]

\[
= (2\hbar/iL)(n\pi/L) \int_0^L \sin(n\pi x / L) \cos(n\pi x / L) dx = 0
\]

Also, note that

\[
\langle p^2 \rangle_n = 2mE_n = n^2\hbar^2/4L^2
\]

Thus,

\[
\Delta p_n = \{\langle p^2 \rangle_n - \langle p \rangle_n^2\}^{1/2} = \langle p^2 \rangle_n^{1/2} = n\hbar/2L
\]

Therefore:

\[
\Delta x_n\Delta p_n = (L/2\sqrt{3})\{1 - (6/n^2\pi^2)\}^{1/2}(n\hbar/2L)
\]

\[
= (n/4\sqrt{3})\{1 - (6/n^2\pi^2)\}^{1/2}h = (n\pi / \sqrt{3})\{1 - (6/n^2\pi^2)\}^{1/2}(h/2)
\]

\[
\Delta x_2\Delta p_2 = (2\pi / \sqrt{3})\{1 - (3/2\pi^2)\}^{1/2}(h/2) = 3.3406(h/2) > h/2
\]

as required. As \( n \) increases, the uncertainty product \( \Delta x_n\Delta p_n \) increases.

**Exercise:** Repeat the calculation for the mixed state \( \psi_1 \cos \beta + \psi_2 \sin \beta \).

What value of \( \beta \) minimizes the uncertainty product?

1.6 To use the Born interpretation to find the probability, we need to first normalize the wavefunction, \( \psi(x) = Ne^{-2x} \). Normalization requires that

\[
\int_0^\infty \psi^* \psi \ dx = \int_0^\infty N^2 e^{-4x} \ dx = 1
\]

which yields \( N = 2 \). The probability of finding the particle at a distance \( x \geq 1 \) is given by
Probability = \int_1^\infty (2e^{-2x})^2 \, dx \\
= e^{-4}

**Exercise:** Suppose that the particle is now described by the unnormalized wavefunction \( \psi(x) = e^{-3x} \). Between 0 and what other distance is the probability of finding the particle equal to \( \frac{1}{2} \)?

1.7 Use eqn 1.44. Since \( l_z = (\hbar/i)(\partial/\partial \phi) \), \( V(\phi) = V \), a constant, and \( H = (1/2mr^2)l_z^2 + V \):

\[ [H, l_z] = (1/2mr^2)[l_z^2, l_z] + [V, l_z] = 0 \quad \{[V, l_z] \propto dV/d\phi = 0\}, \]

Hence, \( \langle d/dt l_z \rangle = 0 \)

**Exercise:** Find the equation of motion for the expectation value of \( l_z \) for a particle on a vertical ring in a uniform gravitational field. Examine the equations for small displacements from the lowest point.

1.8 The most probable location is given by the value of \( x \) corresponding to the maximum (or maxima) of \( |\psi|^2 \); write this location \( x^* \). In the present case

\[ |\psi|^2 = N^2 x^2 e^{-x^2/\Gamma^2} \]

\[ (d/dx)|\psi|^2 = N^2 \{2xe^{-x^2/\Gamma^2} - 2(x^3/\Gamma^2)e^{-x^2/\Gamma^2}\} = 0 \text{ at } x = x^* \]

Hence, \( 1 - x^2/\Gamma^2 = 0, \) so \( x^* = \pm \Gamma \)

**Exercise:** Evaluate \( N \) for the wavefunction. Consider then another excited state wavefunction \( \{2(x/\Gamma)^2 - 1\} e^{-x^2/2\Gamma^2} \), and locate \( x^* \).

1.9 Base the answer on \( |\psi|^2 = (b^3/\pi)e^{-2br} \). The probability densities are

(a) \( |\psi(0)|^2 = b^3/\pi = 1/(53 \text{ pm})^3 \pi = 2.1 \times 10^{-6} \text{ pm}^{-3} \)

(b) \( |\psi(r = 1/b, \theta, \phi)|^2 = (b^3/\pi)e^{-2} = 2.9 \times 10^{-7} \text{ pm}^{-3} \)
[The values of \( \theta \) and \( \phi \) do not matter because \( \psi \) is spherically symmetrical.] The probabilities are given by

\[
P = \int_{\text{volume}} \psi^2 d\tau \approx |\psi|^2 \delta V
\]

because \( |\psi|^2 \) is virtually constant over the small volume of integration \( \delta V = 1 \text{ pm}^3 \).

Hence:

(a) \( P = |\psi(0)|^2 \delta V = 2.1 \times 10^{-6} \);

(b) \( P = |\psi(1/b, \theta, \phi)|^2 \delta V = 2.9 \times 10^{-7} \)

Problems

1.1  (a)

\[
\langle p_x \rangle \propto \left< \sin(\pi x/L) \right| \frac{d}{dx} \left| \sin(\pi x/L) \right> \propto \left< \sin(\pi x/L) \right| \cos(\pi x/L) = 0
\]

(b)

\[
\langle p_x^2 \rangle = 2m\langle T \rangle = 2mE [V = 0] \quad \text{[see eqn 2.30]}
\]

\[
= 2m \left( \frac{\hbar^2}{8mL^2} \right) \quad \text{[for } n = 1] = \frac{\hbar^2}{4L^2}
\]

Alternatively, integrate explicitly.

Exercise: Evaluate (a) \( \langle p_x^3 \rangle \), (b) \( \langle p_x^4 \rangle \).

1.4  (a) \([A, B] = AB - BA = -(BA - AB) = -[B, A]\)

(b) \([A^m, A^n] = A^m A^n - A^n A^m = A^{m+n} - A^{m+n} = 0\)
(c) \[
[A^2, B] = AAB - BAA = ABA + (AAB - ABA) - ABA + (ABA - BAA) \\
= A[A, B] + [A, B]A
\]

(d) \[
[A, [B, C]] + [B, [C, A]] + [C, [A, B]] \\
= (ABC - ACB - BCA + CBA) + (BCA - BAC - CAB + ACB) \\
+ (CAB - CBA - ABC + BAC) = 0
\]

**Exercise:** Express \([A^2, B]^2\), \([A^3, B]\), and \([A, [B, [C, [D, E]]]]\) in terms of individual commutators.

1.7 Find a normalization constant \(N\) such that eqn 1.18 is satisfied.

\[
\int |\psi|^2 d\tau = N^2 \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 e^{-2br} dr \\
= N^2 \{2\pi\} \{2\} \int_0^\infty r^2 e^{-2br} dr = 4\pi N^2 \{2!/(2b)^3\} \\
= N^2 \pi/b^3.
\]

Hence \(N = (b^3/\pi)^{1/2} = 1.5 \times 10^{15} \text{ m}^{-3/2}\)

Consequently, \(\psi = (b^3/\pi)^{1/2} e^{-br}\)

**Exercise:** \(\psi\) depends on \(Z\) as \(e^{-2br}\). Find \(N\) for general \(Z\).

1.10 (a) \([1/x, p_x]\); use the position representation.
\[ [1/x, p_x] = [x^{-1}, (\hbar/i) d/dx] = (\hbar/i) \{ x^{-1} (d/dx) - (d/dx) x^{-1} \} \]
\[ = (\hbar/i) \{ x^{-1} (d/dx) - (d^{-1}/dx) - x^{-1} (d/dx) \} \]
\[ = -(\hbar/i) \frac{d}{dx} x^{-1} = (\hbar/i) x^{-2} \]

(b)

\[ [1/x, p_x^2] = [x^{-1}, -\hbar^2 (d^2/dx^2)] \]
\[ = -\hbar^2 \{ x^{-1} (d^2/dx^2) - (d^2/dx^2) x^{-1} \} \]
\[ = -\hbar^2 \{ x^{-1} (d^2/dx^2) - (d/dx) [(d^{-1}/dx) + x^{-1} (d/dx)] \} \]
\[ = -\hbar^2 \{ x^{-1} (d^2/dx^2) - (d/dx) [-x^{-2} + x^{-1} (d/dx)] \} \]
\[ = -\hbar^2 \{ x^{-1} (d^2/dx^2) + (d^{-2}/dx) + x^{-2} (d/dx) \} \]
\[ = -\hbar^2 \{ -2x^{-3} + 2x^{-2} (d/dx) \} \]
\[ = 2\hbar^2/x^3 - 2\hbar^2 x^{-2} (i/\hbar) p_x = (2\hbar/x^3) (\hbar - i x p_x) \]

(c)

\[ [xp_y - yp_z, yp_z - zp_x] \]
\[ = [xp_y, yp_z] - [xp_y, zp_x] - [yp_z, yp_z] + [yp_z, zp_x] \]
\[ = x[p_y, y] p_z - 0 - 0 + p_x[y, p_z]z \]
\[ = x(-i\hbar) p_z + p_x(i\hbar) z = i\hbar(z p_x - x p_x) \]

(d)
\[\begin{align*}
[x^2(\partial^2/\partial y^2), y(\partial/\partial x)] \\
&= x^2(\partial^2/\partial y^2)y(\partial/\partial x) - y(\partial/\partial x)x^2(\partial^2/\partial y^2) \\
&= x^2(\partial/\partial x)(\partial^2/\partial y^2)y - (\partial/\partial x)x^2y(\partial^2/\partial y^2) \\
&= x^2(\partial/\partial x)(\partial/\partial y)\{1 + y(\partial/\partial y)\} - \{2x + x^2(\partial/\partial x)\}y(\partial^2/\partial y^2) \\
&= 2x^2(\partial/\partial x)(\partial/\partial y) - 2xy(\partial^2/\partial y^2) \\
&= 2x^2(\partial^2/\partial x\partial y) - 2xy(\partial^2/\partial y^2).
\end{align*}\]

**Exercise:** Evaluate \([xy(\partial^2/\partial x\partial y), x^2(\partial^2/\partial y^2)]\).

**1.13** Use the correspondence in Section 1.5.

(a)

\[T = p^2/2m = -(\hbar^2/2m)(\partial^2/\partial x^2)\] in one dimension.

\[T = p^2/2m = -(\hbar^2/2m)\{(\partial^2/\partial x^2) + (\partial^2/\partial y^2) + (\partial^2/\partial z^2)\} = -(\hbar^2/2m)\nabla^2\] in three dimensions.

(b) \(1/x \rightarrow \text{multiplication by } (1/x)\)

(c) \(\mu = \sum_i Q_i r_i \rightarrow \text{multiplication by } \sum_i Q_i r_i\)

(d)

\[l_z = xp_y - yp_x = (\hbar/\iota)\{x(\partial/\partial y) - y(\partial/\partial x)\} = (\hbar/\iota)(\partial/\partial \phi)\] for \(x = r \cos \phi, y = r \sin \phi\)

(e) \(\partial x^2 = x^2 - \langle x \rangle^2 \rightarrow \text{multiplication by } \{x^2 - \langle x \rangle^2\}\)

\[\partial p_x = p^2 - \langle p \rangle^2 \rightarrow \{-\hbar^2(\partial^2/\partial x^2) - \langle p \rangle^2\}\]

**Exercise:** Devise operators for \(1/r, xp_x\), and \(e^{\alpha x}\).
1.16 Take $H\Psi = \kappa (\partial^2 \Psi / \partial t^2)$. Because $H$ has the dimensions of energy, $\kappa$ must have the dimensions of energy $\times$ time$^2$, or ML$^2$. Try $\Psi = \psi \theta$, with $H$ an operator on $x$, not $t$. The equation separates into $H\psi = E\psi$, $\partial^2 \theta / \partial t^2 = (E/\kappa)\theta$. The latter admits solutions of the form $\theta \propto \cos (E/\kappa)^{1/2} t$. Then

$$\int |\Psi|^2 \, d\tau \propto \int |\psi|^2 \, d\tau \cos^2 (E/\kappa)^{1/2} t$$

which oscillates in time between 0 and 1; hence the total probability is not conserved.

1.19  (a)

$$e^A e^B = (1 + A + \frac{1}{2} A^2 + \ldots)(1 + B + \frac{1}{2} B^2 + \ldots) = 1 + (A + B) + \frac{1}{2} (A^2 + 2AB + B^2) + \ldots$$

$$e^{A+B} = 1 + (A + B) + \frac{1}{2} (A + B)^2 + \ldots = 1 + (A + B) + \frac{1}{2} (A^2 + 2AB + BA + B^2) + \ldots$$

Therefore, $e^A e^B = e^{A+B}$ only if $AB = BA$, which is so if $[A, B] = 0$.

(b) If $[A, [A, B]] = [B, [A, B]] = 0$, then
\[ e^{A+B} = 1 + (A + B) + \frac{1}{2}(A^2 + AB + BA + B^2) \]
\[ + (1/3!)(A^3 + A^2B + ABA + BAA + BAB + BAB + B^3) + \ldots \]
\[ = 1 + (A + B) + \frac{1}{2}(A^2 + 2AB + B^2) - \frac{1}{2}[A, B] \]
\[ + (1/3!)(A^3 + 3A^2B + 3AB^2 + B^3) - \frac{1}{2}(A + B)[A, B] + \ldots \]
\[ = e^A e^B e^{-\frac{1}{2}[A, B]} \]

Therefore, \( e^A e^B = e^{A+B} e^f \) where \( f = [A, B]/2 \).

**Exercise:** Find expressions for \( \cos A \cos B \) and \( \cos A \sin B \), where \( A \) and \( B \) are operators such that

\[ [A, [A, B]] = [B, [A, B]] = 0 \]

(Use \( \cos A = \frac{1}{2}(e^{iA} + e^{-iA}) \), etc.)

**1.22** \( (d/dt)\langle \Omega \rangle = (i/\hbar)\langle [H, \Omega] \rangle \) [eqn 1.44].

For a harmonic oscillator, \( H = \frac{p_x^2}{2m} + \frac{1}{2}k_x x^2 \), and

\[ [H, x] = [p_x^2/2m, x] = -(i \hbar /m)p_x \quad \text{[Problem 1.11]} \]
\[ [H, p_x] = [\frac{1}{2} k_x x^2, p_x] = -i \hbar k_x x \quad \text{[Problem 1.11]} \]

\( (d/dt)\langle x \rangle = (1/m)\langle p_x \rangle ; (d/dt)\langle p_x \rangle = -k_x \langle x \rangle \)

Therefore

\[ (d^2/dt^2)\langle x \rangle = (1/m)(d/dt)\langle p_x \rangle = -(k_x/m)\langle x \rangle \]

The solution of \( (d^2/dt^2)\langle x \rangle = -(k_x/m)\langle x \rangle \) is
\[ \langle x \rangle = A \cos \omega t + B \sin \omega t, \quad \omega^2 = k \epsilon / m \]

\[ \langle p \rangle = m (d/dt) \langle x \rangle = -Am \omega \sin \omega t + Bm \omega \cos \omega t \]

which is the classical trajectory.

**Exercise:** Find the equation of motion of the expectation values of \( x \) and \( p \) for a quartic oscillator \( (V \propto x^4) \).

**1.25** \((-\hbar^2/2m)(d^2\Psi/dx^2) + V(t)\Psi = i\hbar(\partial\Psi/\partial t)\).

(a) Try \( \Psi = \varphi(x)\theta(t) \), then

\[ (-\hbar^2/2m)\varphi'' \theta + V(t)\varphi \theta = i\hbar \varphi \partial \varphi/\partial t \]

\[ -(\hbar^2/2m)(\varphi''/\varphi) + V(t) - i\hbar (\partial \theta/\partial t) (1/\varphi) = 0 \]

By the same argument as that in Section 1.14, \((-\hbar^2/2m)(\varphi''/\varphi) = \epsilon \), a constant; hence

\[ \varphi'' = -(2m\epsilon/\hbar^2)\varphi \]

(1.1)

\[ i\hbar (\partial \theta/\partial t) (1/\varphi) - V(t) = \epsilon \], the same constant; hence

\[ (d/dt) \ln \theta = \epsilon + V(t)/i\hbar \]

(1.2)

(b) Equation (1) has the solution \( \psi = Ae^{ikx} + Be^{-ikx} \), \( k = (2m\epsilon/\hbar^2)^{1/2} \)

Equation (2) has the solution \( \ln \theta (t) = \ln \theta (0) - (i/\hbar) \int_0^t \{ \epsilon + V(t) \} \, dt \)

Therefore, on absorbing \( \ln \theta (0) \) into \( A \) and \( B \),

\[ \Psi = \varphi(x) \exp \left\{ -i(\epsilon / \hbar)t - (i/\hbar) \int_0^t V(t) \, dt \right\} \]
Let \( V(t) = V \cos \omega t \), then \( \int_0^t V(t)dt = (V/\omega) \sin \omega t \), so

\[
\Psi = \psi(x) \exp \{ -i(\varepsilon/\hbar)t - i(V/\hbar \omega) \sin \omega t \}
\]

\[
= \psi(x)(\cos \phi - i \sin \phi), \quad \phi = \alpha/\hbar + (V/\hbar \omega) \sin \omega t.
\]

The behaviour of the real and imaginary parts of \( \Psi \) (essentially the functions \( \cos(\tau + \sin \tau) \) and \( \sin(\tau + \sin \tau) \)) is shown in Fig. 1.1. The dotted line is \( \cos(\tau + \sin \tau) \) and the full line is \( \sin(\tau + \sin \tau) \).

![Figure 1.1: The real (dotted line) and imaginary (full line) components of \( \Psi \).](image)

\textbf{(c)} Note that \( |\Psi|^2 = |\psi(x)|^2 \), and so it is stationary.
**Exercise:** Consider the form of $\Psi$ for an exponentially switched cosine potential energy, $V(t) = V(1 - e^{-t/T}) \cos \omega t$, for various switching rates.

1.28 From eqn 1.44,

$$\frac{d\langle x \rangle}{dt} = \frac{i}{\hbar} \langle [H, x] \rangle$$

The commutator has been evaluated in Problem 1.11(b):

$$\langle [H, x] \rangle = \frac{\hbar}{im} p_x$$

and therefore

$$\frac{d\langle x \rangle}{dt} = \frac{\langle p_x \rangle}{m}$$

which is eqn 1.47.