Chapter 1

The foundations of quantum mechanics

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Exercises

- 1.1 (a) $\int (f+g)dx = \int fdx + \int gdx$; linear.
 - **(b)** $(f+g)^{1/2} \neq f^{1/2} + g^{1/2}$; <u>nonlinear</u>.
 - (c) f(x+a) + g(x+a) = f(x+a) + g(x+a); linear.
 - (d) f(-x) + g(-x) = f(-x) + g(-x); <u>linear</u>.

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

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

$$(d/dx)e^{ax^2} = 2axe^{ax^2} = 2a\{xe^{ax^2}\}; e^{ax^2} \text{ not an e.f.}$$

- (d/dx)x = 1; x not an e.f.
- $(d/dx)x^2 = 2x; x^2$ not an e.f.
- (d/dx)(ax + b) = a; ax + b not an e.f.
- $(d/dx)\sin x = \cos x$; $\sin x$ not an e.f.
- **(b)** $(d^2/dx^2)e^{ax} = a^2e^{ax}$; e^{ax} is an eigenfunction, eigenvalue a^2 .

$$(d^2/dx^2)e^{ax^2} = 2ae^{ax^2} + 4a^2x^2e^{ax^2}; e^{ax^2} \text{ not an e.f.}$$

- $(d^2/dx^2)x = 0 = 0x$; x is an e.f.; e.v. is 0.
- $(d^2/dx^2)x^2 = 2$; x^2 not an e.f.
- $(d^2/dx^2)(ax + b) = 0 = 0(ax + b); ax + b is an e.f.; e.v. is 0.$
- $(d^2/dx^2)\sin x = -\sin x$; sin x is an 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^{2^2} .

1.3

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

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 Δx , 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 × 10⁻²⁵ kg m s⁻¹)/(9.109 38 × 10⁻³¹ kg)
= 5.8 × 10⁵ m s⁻¹

(b) Since, $E_{\rm K} = p_x^2 / 2m_{\rm e}$

$$\Delta E_{\rm K} = (\Delta p_x)^2 / 2m_{\rm e}$$

= (5.3 × 10⁻²⁵ kg m s⁻¹)²/(2 × 9.109 38 × 10⁻³¹ kg)
= 1.5 × 10⁻¹⁹ 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

$$\int x^{2} \sin^{2} ax dx = \frac{1}{6} x^{3} + (1/4a^{3}) \{ \frac{1}{2} \sin(2ax) - ax \cos(2ax) - a^{2}x^{2} \sin(2ax) \}$$
$$\langle x^{2} \rangle_{n} = (2/L) \int_{0}^{L} x^{2} \sin^{2}(n\pi x/L) dx = \frac{1}{3} L^{2} \{ 1 - (3/2n^{2}\pi^{2}) \}$$
$$\langle x^{2} \rangle_{2} = \frac{1}{3} L^{2} \{ 1 - (3/8\pi^{2}) \}$$

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,

$$\Delta x_n = \{ \langle x^2 \rangle_n - \langle x \rangle_n^2 \}^{1/2} = \{ \frac{1}{3} L^2 - (1/2n^2 \pi^2) L^2 - \frac{1}{4} L^2 \}^{1/2}$$
$$= \frac{(L/2\sqrt{3})\{1 - (6/n^2 \pi^2)\}^{1/2}}{\Delta x_2} = (L/2\sqrt{3})\{1 - (3/2\pi^2)\}^{1/2}$$

As for the momentum, the intuitive solution is $\langle p \rangle_n = 0$ because the wavefunction is a standing wave. The elegant solution is

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$$\langle p \rangle = \langle n | p | n \rangle = \langle n | p | n \rangle^*$$
 [hermiticity] = $\langle n | p^* | n \rangle = -\langle n | p | n \rangle [p^* = -p].$

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

$$\langle p^2 \rangle_n = 2mE_n = \frac{n^2h^2/4L^2}{4L^2}$$

Thus,

$$\Delta p_n = \left\{ \langle p^2 \rangle_n - \langle p \rangle_n^2 \right\}^{1/2} = \langle p^2 \rangle_n^{1/2} = \underline{nh/2L}$$

Therefore:

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

= $(n/4\sqrt{3}) \{1 - (6/n^2 \pi^2)\}^{1/2} \hbar = (n\pi/\sqrt{3}) \{1 - (6/n^2 \pi^2)\}^{1/2} (\hbar/2)$
 $\Delta x_2 \Delta p_2 = (2\pi/\sqrt{3}) \{1 - (3/2\pi^2)\}^{1/2} (\hbar/2) = \underline{3.3406(\hbar/2)} > \hbar/2$

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 β 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

$$\int_0^\infty \psi * \psi \, \mathrm{d}x = \int_0^\infty N^2 \mathrm{e}^{-4x} \mathrm{d}x = 1$$

which yields N = 2. The probability of finding the particle at a distance $x \ge 1$ 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 \{ [V, l_z] \propto dV/d\phi = 0 \},\$$

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

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

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

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

(b) $|\psi(r = 1/b, \theta, \phi)|^2 = (b^3/\pi)e^{-2} = \underline{2.9 \times 10^{-7} \text{ pm}^{-3}}$

[The values of θ and ϕ do not matter because ψ 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)
$$P = |\psi(0)|^2 \delta V = \underline{2.1 \times 10^{-6}};$$

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

Problems

1.1 (a)

$$\langle p_x \rangle \propto \langle \sin(\pi x/L) \left| \frac{d}{dx} \right| \sin(\pi x/L) \rangle$$

 $\propto \langle \sin(\pi x/L) | \cos(\pi x/L) \rangle = 0$

(b)

$$\langle p_x^2 \rangle = 2m\langle T \rangle = 2mE [V=0]$$
 [see eqn 2.30]

$$=2m\left(\frac{h^2}{8mL^2}\right)$$
 [for $n = 1$] $= \frac{h^2/4L^2}{2}$

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)

$$[A2, B] = AAB - BAA = ABA + (AAB - ABA) - ABA + (ABA - BAA)$$
$$= A[A, B] + [A, B]A$$

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

Exercise: ψ depends on Z as e^{-Zbr} . Find N for general Z.

1.10 (a) $[1/x, p_x]$; use the position representation.

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

(b)

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

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

(c)

$$[xp_{y} - yp_{x}, yp_{z} - zp_{y}]$$

= $[xp_{y}, yp_{z}] - [xp_{y}, zp_{y}] - [yp_{x}, yp_{z}] + [yp_{x}, zp_{y}]$
= $x[p_{y}, y]p_{z} - 0 - 0 + p_{x}[y, p_{y}]z$
= $x(-i\hbar)p_{z} + p_{x}(i\hbar)z = i\hbar(zp_{x} - xp_{z})$

(d)

$$[x^{2}(\partial^{2}/\partial y^{2}), y(\partial/\partial x)]$$

$$= x^{2}(\partial^{2}/\partial y^{2})y(\partial/\partial x) - y(\partial/\partial x)x^{2}(\partial^{2}/\partial y^{2})$$

$$= x^{2}(\partial/\partial x)(\partial^{2}/\partial y^{2})y - (\partial/\partial x)x^{2}y(\partial^{2}/\partial y^{2})$$

$$= x^{2}(\partial/\partial x)(\partial/\partial y) \{1 + y(\partial/\partial y)\} - \{2x + x^{2}(\partial/\partial x)\}y(\partial^{2}/\partial y^{2})$$

$$= x^{2}(\partial/\partial x)\{2(\partial/\partial y) + y(\partial^{2}/\partial y^{2})\} - 2xy(\partial^{2}/\partial y^{2}) - x^{2}(\partial/\partial x)y(\partial^{2}/\partial y^{2})$$

$$= 2x^{2}(\partial/\partial x)(\partial/\partial y) - 2xy(\partial^{2}/\partial y^{2})$$

$$= 2x^{2}(\partial^{2}/\partial x\partial y) - 2xy(\partial^{2}/\partial y^{2})$$

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)

$$T = p^2/2m = -(\hbar^2/2m)(d^2/dx^2) \text{ in one dimension.}$$
$$T = p^2/2m = -(\hbar^2/2m)\{(\partial^2/\partial x^2) + (\partial^2/\partial y^2) + (\partial^2/\partial z^2)\}$$
$$= -(\hbar^2/2m)\nabla^2 \text{ in three dimensions.}$$

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

(c)
$$\mu = \sum_{i} Q_{i} \mathbf{r}_{i} \rightarrow \text{multiplication by } \sum_{i} Q_{i} \mathbf{r}_{i}$$

(d)

$$l_z = xp_y - yp_x = (\hbar/i) \{ x(\partial/\partial y) - y(\partial/\partial x) \}$$
$$= (\hbar/i)(\partial/\partial \phi) \text{ for } x = r \cos \phi, y = r \sin \phi$$

 ϕ

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

 $\delta p^2 = p^2 - \langle p \rangle^2 \rightarrow \{-\hbar^2(\partial^2/\partial x^2) - \langle p \rangle^2\}$

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, κ must have the dimensions of energy \times time², or ML². Try $\Psi = \psi \theta$, with *H* an operator on *x*, not *t*. The equation separates into $H\psi = E\psi$, $d^2\theta/dt^2 = (E/\kappa)\theta$. The latter admits solutions of the form $\theta \propto \cos(E/\kappa)^{1/2}t$. Then

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

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

1.19 (a)

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

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!)(A³ + A²B + ABA + BAA + BBA + BAB + ABB + B³) + ...
= 1 + (A + B) + \frac{1}{2}(A^2 + 2AB + B^2) - \frac{1}{2}[A, B]
+ (1/3!)(A³ + 3A²B + 3AB² + B³) - $\frac{1}{2}(A + B)[A, B] + ...$
= $e^A e^B e^{-\frac{1}{2}[A,B]}$

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, $H = p_x^2/2m + \frac{1}{2}k_f x^2$, and

 $[H, x] = [p_x^2/2m, x] = -(i \hbar / m)p_x$ [Problem 1.11]

$$[H, p_x] = [\frac{1}{2} k_f x^2, p_x] = -i \hbar k_f x$$
 [Problem 1.11]

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

Therefore

$$(d^2/dt^2)\langle x \rangle = (1/m)(d/dt)\langle p_x \rangle = -(k_f/m)\langle x \rangle$$

The solution of $(d^2/dt^2)\langle x \rangle = -(k_f/m)\langle x \rangle$ is

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 $\langle x \rangle = A \cos \omega t + B \sin \omega t, \quad \omega^2 = k_f / m$ $\langle p \rangle = m(d/dt) \langle x \rangle = -Am\omega \sin \omega t + Bm\omega \cos \omega t$

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 $\Psi = \psi(x) \theta(t)$, then

$$(-\hbar^2/2m)\psi''\theta + V(t)\psi\theta = i\hbar\psi d\theta/dt$$
$$-(\hbar^2/2m)(\psi''/\psi) + V(t) - i\hbar(d\theta/dt)(1/\theta) = 0$$

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

$$\psi'' = -(2m\varepsilon/\hbar^2)\psi \tag{1.1}$$

i $\hbar (d\theta/dt) (1/\theta) - V(t) = \varepsilon$, the same constant; hence

$$(d/dt) \ln \theta = \varepsilon + V(t)/i\hbar$$
 (1.2)

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

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

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

$$\Psi = \psi(x) \exp\left\{-i(\varepsilon/\hbar)t - (i/\hbar)\int_0^t V(t)dt\right\}$$

Let $V(t) = V \cos \omega t$, then $\int_0^t V(t) dt = (V/\omega) \sin \omega t$, so

$$\Psi = \psi(x) \exp\{-i(\varepsilon/\hbar)t - i(V/\hbar\omega)\sin\omega t\}$$
$$= \psi(x)(\cos\phi - i\sin\phi), \ \phi = \varepsilon t/\hbar + (V/\hbar\omega)\sin\omega t.$$

The behaviour of the real and imaginary parts of Ψ (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 $\sin(\tau + \sin \tau)$.

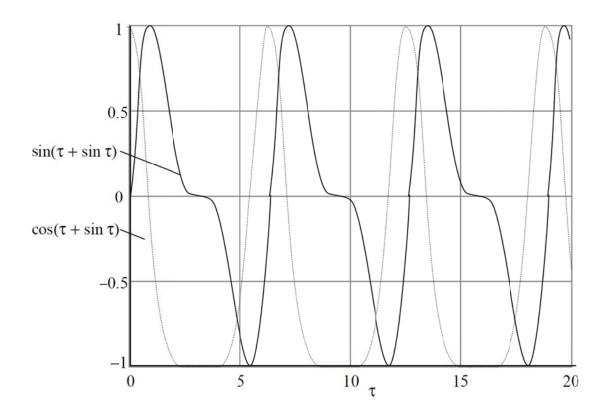


Figure 1.1: The real (dotted line) and imaginary (full line) components of Ψ .

(c) Note that $|\Psi|^2 = |\psi(x)|^2$, and so it is stationary.

Exercise: Consider the form of Ψ 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,

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

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

$$\langle [H, x] \rangle = \frac{\hbar}{\mathrm{i}m} p_x$$

and therefore

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

which is eqn 1.47.