Momentum Operators
for
Particle-in-a-Box Problems

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Introduction. Let me describe the little conundrum that served originally to motivated this discussion. A particle of mass m is confined to the interior of a one-dimensional box: $0 < x < a$. The quantum theory of this simplest of all quantum systems standardly proceeds from

$$\frac{1}{2m}\Big(\frac{\hbar}{i}\frac{\partial}{\partial x}\Big)^2\psi(x) = E\,\psi(x) \quad : \quad \psi(0) = \psi(a) = 0$$

One is led[1] to eigenvalues

$$E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2 \quad : \quad n = 1, 2, 3, \ldots$$

and to normalized energy eigenfunctions

$$\psi_n(x) = \sqrt{2/a}\,\sin\big(n\pi x/a\big)$$

The normalized wavefunction

$$\Psi(x) = \sqrt{30/a^5}\,x(a-x)$$

does obviously satisfy the boundary conditions $\Psi(0) = \Psi(a) = 0$, but is *not* an eigenstate, though it very closely resembles the ground state when plotted.

One expects to have—for the energy as for any other observable—

$$\text{var}_\psi(\mathsf{H}) \equiv \big\langle[\mathsf{H} - \langle\mathsf{H}\rangle]^2\big\rangle = \big\langle\mathsf{H}^2\big\rangle - \langle\mathsf{H}\rangle^2$$

[1] Griffiths, *Introduction to Quantum Mechanics* (2^{nd} edition, 2005), page 32.

If the system is an energy eigenstate then—because the energy is precisely known—one expects the variance to vanish, and indeed

$$\mathrm{var}_{\psi_n}(\mathbf{H}) = E_n^2 - (E_n)^2 = 0$$

For other states ψ we expect to have

$$\mathrm{var}_{\psi}(\mathbf{H}) > 0 \quad : \quad \psi \text{ not an energy eigenstate}$$

Look, however, to the quadratic state Ψ. If we

$$\text{interpret } \mathbf{H}^2 \text{ to mean } \Big[\frac{1}{2m}\Big(\frac{\hbar}{i}\frac{\partial}{\partial x}\Big)^2\Big]^2 \tag{1}$$

we are led to write (since $\Psi(x)$ vanishes when differentiated three or more times) $\big\langle \mathbf{H}^2\big\rangle = 0$, and thus to the absurd result

$$\mathrm{var}_{\Psi}(\mathbf{H}) = 0 - \langle \mathbf{H}\rangle^2 = 0 - \Big(\frac{5\hbar^2}{ma^2}\Big)^2$$

That there exist contexts in which $\frac{\hbar}{i}\partial_x$ does not serve to represent the momentum operator $\mathbf{p}$ (and in which $[\frac{\hbar}{i}\partial_x]^n$ does not serve to represent powers $\mathbf{p}^n$ of the momentum operator) has been frequently noted, and came forcibly to my own attention while writing the final pages of "E. T. Whittaker's quantum formalism" (2001). I make reference there to (among other papers) Peter D. Robinson & Joseph O. Hirschfelder, "Generalized momentum operators in quantum mechanics," J. Math. Phys. **4**, 338 (1963) and Peter D. Robinson, "Integral forms for quantum-mechanical momentum operators," J. Math. Phys. **7**, 2060 (1966), and it is on Robinson's work that I base the present discussion.

Why self-adjointness demonstrations sometimes fail. The one-dimensional free particle problem directs our attention to the space $\mathcal{H}$ of functions that are defined and square-integrable on the real line: $x \in (-\infty, +\infty)$. Assuming the inner product to be defined

$$(\phi, \psi) \equiv \int_{-\infty}^{+\infty} \phi^*(x)\psi(x)\,dx$$

we have

$$\begin{aligned}(\phi, i\partial\psi) &= \int_{-\infty}^{+\infty} \phi^*(x)[i\partial\psi(x)]\,dx\\ &= \underbrace{i\,\phi^*(x)\psi(x)\Big|_{-\infty}^{+\infty}}_{\text{boundary term}} - \int_{-\infty}^{+\infty} [i\,\partial\phi^*(x)]\psi(x)\,dx\\ &= \text{boundary term} + \int_{-\infty}^{+\infty} [i\,\partial\phi(x)]^*\psi(x)\,dx\\ &= (i\partial\phi, \psi)\end{aligned}$$

We have Similarly

$$
\begin{aligned}
(\phi,(i\partial)^2\psi) &= i\,\phi^*(x)[i\partial\psi(x)]\Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}[i\partial\phi^*(x)][i\partial\psi(x)]\,dx\\
&= i\,\phi^*(x)[i\partial\psi(x)]\Big|_{-\infty}^{+\infty} - i[i\partial\,\phi^*(x)]\psi(x)\Big|_{-\infty}^{+\infty}\\
&\qquad\qquad + \int_{-\infty}^{+\infty}[(i\partial)^2\phi^*(x)]\psi(x)\,dx\\
&= \text{two boundary terms} + \int_{-\infty}^{+\infty}[(i\partial)^2\phi(x)]^*\psi(x)\,dx\\
&= ((i\partial)^2\phi,\psi)\\
&\;\;\vdots\\
(\phi,(i\partial)^n\psi) &= ((i\partial)^n\phi,\psi)
\end{aligned}
$$

The self-adjointness of all the differential operators $(i\,\partial)^n$ is seen thus to follow from the presumption that all the elements of $\mathcal{H}$ vanish (together with their derivatives of all orders) at $x\to\pm\infty$, which would appear to follow from the normalizability requirement (though David Griffiths remarks somewhere that there exist normalizable functions on the real line that do *not* vanish at infinity).

If the particle is constrained to move on a ring they we expect $\psi(x)\in\mathcal{H}$ and all of its derivatives to be periodic—a condition that serves even less problematically to kill all all boundary terms.

Problems arise, however, if the particle is constrained to move on a finite interval (confined to the interior of a box): $x\in[a,b]$. For while we can expect to have $\psi(a)=\psi(b)=0$, we cannot expect to have $\psi^{(n)}(a)=\psi^{(n)}(b)$. Look, for example, to the energy eigenfunctions

$$\psi_n(x)=\sqrt{2/a}\,\sin\big(n\pi x/a\big)$$

of a particle confined to the interior of the box $x\in[0,a]$. For such functions we have

$$
\begin{aligned}
\psi_n^{(k)}(0) &= \;\;\psi_n^{(k)}(a)=0 &&:\quad k\text{ even, all }n\\
\psi_n^{(k)}(0) &= +\psi_n^{(k)}(a)\neq 0 &&:\quad k\text{ odd, }n\text{ even}\\
\psi_n^{(k)}(0) &= -\psi_n^{(k)}(a)\neq 0 &&:\quad k\text{ odd, }n\text{ odd}
\end{aligned}
$$

And if we take into account the notion that the eigenfunctions *vanish outside the box* then the derivatives of all orders become discontinuous (ill-defined) at $x=0$ and $x=a$.

Notational simplifications. It is to minimize notational clutter that I set

$$\hbar=1,\quad 2m=1,\quad a=1$$

The time-independent Schrödinger equations now reads

$$(i\partial_x)^2\psi(x)=E\psi(x)\quad:\quad \psi(0)=\psi(1)=0$$

The energy eigenvalues have become

$$E_n=\pi^2n^2\quad:\quad n=1,2,3,\ldots$$

The eigenfunctions have become

$$\psi_n(x) = \sqrt{2}\sin(n\pi x)$$

and span a function space $\mathcal{H}_0$ all elements of which vanish at the boundaries of the unit interval. But application of the $i\partial_x$ operator yields functions

$$i\partial\psi_n(x) = i\sqrt{2}\,n\pi\cos(n\pi x)$$

that do not vanish at the boundaries of the unit interval, functions that are not elements of $\mathcal{H}_0$, that are elements of $\mathcal{H}\supset\mathcal{H}_0$. We have

$$\begin{aligned}(\phi, i\partial\psi) &= \int_0^1 \phi^*(x)[i\partial\psi(x)]\,dx\\ &= \underbrace{i\,\phi^*(x)\psi(x)\Big|_0^1}_{\text{boundary term}} - \int_0^1 [i\,\partial\phi^*(x)]\psi(x)\,dx\\ &= i\,\phi^*(1)\psi(1) - i\,\phi^*(0)\psi(0) + \int_0^1 [i\,\partial\phi(x)]^*\psi(x)\,dx\end{aligned}$$

and, since deprived of means to kill the boundary term, must find a way to live with it. We observe in this connection that

$$\begin{aligned}\int_0^1 \delta(x-0)f(x)\,dx &= \tfrac{1}{2}f(0)\\ \int_0^1 \delta(x-1)f(x)\,dx &= \tfrac{1}{2}f(1)\end{aligned}$$

so if we define

$$\Delta(x) \equiv \delta(x-1) - \delta(x-0)$$

we find

$$\int_0^1 \Delta(x)f(x)\,dx = \tfrac{1}{2}f(x)\Big|_0^1$$

$$\begin{aligned}\int_0^1 \phi^*(x)[i\{\partial-\Delta\}\psi(x)]\,dx &= \big(1-\tfrac{1}{2}\big)i\,\phi^*(x)\psi(x)\Big|_0^1 - \int_0^1 [i\,\partial\phi^*(x)]\psi(x)\,dx\\ &= \tfrac{1}{2}i\,\phi^*(x)\psi(x)\Big|_0^1 + \int_0^1 [i\,\partial\phi(x)]^*\psi(x)\,dx\\ &= \int_0^1 [i\,\{\partial-\Delta\}\phi(x)]^*\psi(x)\,dx\end{aligned}$$

The implication is that we restore self-adjointness if we send

$$i\partial_x \quad\longmapsto\quad \wp \equiv i\,\{\partial_x - \Delta(x)\}$$