Solutions to the book:
Ira N. Levine, Quantum Chemistry, 5th edition

Meng-Gen Tsai
plover@gmail.com

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Chapter 1: The Schrödinger Equation

Problem 1.1.

(a) *Calculate the energy of one photon of infrared radiation whose wavelength is* 1064 *nm.*

(b) *An Nd:YAG laser emits a pulse of* 1064*-nm radiation of average power* $5 \times 10^6 W$ *and duration* $2 \times 10^{-8} s$*. Find the number of photons emitted in this pulse. (Recall that* $1W = 1J/s$*.)*

Solution of (a).

$$\begin{aligned} E_{\text{photon}} &= h\nu && \text{(Equation (1.1))} \\ &= \frac{hc}{\lambda} && \text{(Equation (1.3))} \\ &= \frac{(6.626 \times 10^{-34} Js)(2.998 \times 10^8 m/s)}{1064 \times 10^{-9} m} \\ &= 1.867 \times 10^{-19} J. \end{aligned}$$

□

Solution of (b). Total energy in one pulse is $E = (5 \times 10^6 W)(2 \times 10^{-8} s) = 0.1J$. By (a), the energy of one photon $E_{\text{photon}} = 1.867 \times 10^{-19} J$. So the number of photons is

$$n = \frac{E}{E_{\text{photon}}} = \frac{0.1J}{1.867 \times 10^{-19} J} = 5 \times 10^{17}.$$

□

Chapter 3: Operators

Problem 3.6.

Prove that $\hat{A}+\hat{B}=\hat{B}+\hat{A}$.

Two operators $\hat{A}$ and $\hat{B}$ are said to be equal if $\hat{A}f=\hat{B}f$ for all functions f.

Proof.

$$(\hat{A}+\hat{B})f=\hat{A}f+\hat{B}f=\hat{B}f+\hat{A}f=(\hat{B}+\hat{A})f$$

holds for any function f. By definition, $\hat{A}+\hat{B}=\hat{B}+\hat{A}$. □

Problem 3.7.

Let $\hat{D}=d/dx$. *Verify that* $(\hat{D}+x)(\hat{D}-x)=\hat{D}^2-x^2-1$.

Proof.

$$\begin{aligned}((\hat{D}+x)(\hat{D}-x))f &= (\hat{D}+x)((\hat{D}-x)f)\\ &= (\hat{D}+x)(f'-xf)\\ &= (f'-xf)'+x(f'-xf)\\ &= (f''-f-xf')+(xf'-x^2f)\\ &= f''-f-x^2f\\ &= (\hat{D}^2-x^2-1)f\end{aligned}$$

holds for any function f. By definition, $(\hat{D}+x)(\hat{D}-x)=\hat{D}^2-x^2-1$. □

Problem 3.27.

Evaluate the commutators

(a) $[\hat{x},\hat{p}_x]$;

(b) $[\hat{x},\hat{p}_x^2]$;

(c) $[\hat{x},\hat{p}_y]$;

(d) $[\hat{x},\hat{V}(x,y,z)]$;

(e) $[\hat{x},\hat{H}]$, *where the Hamiltonian operator is*

$$\hat{H}=-\frac{\hbar}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z);$$

(f) $[\hat{x}\hat{y}\hat{z}, \hat{p}_x^2]$.

Proof of (a).

$$
\begin{aligned}
[\hat{x}, \hat{p}_x]f &= (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})f \\
&= (\hat{x}\hat{p}_x)f - (\hat{p}_x\hat{x})f \\
&= (\hat{x})\left(\frac{\hbar}{i}\frac{\partial f}{\partial x}\right) - (\hat{p}_x)(xf) \\
&= x\frac{\hbar}{i}\frac{\partial f}{\partial x} - \frac{\hbar}{i}\left(f + x\frac{\partial f}{\partial x}\right) \\
&= -\frac{\hbar}{i}f
\end{aligned}
$$

holds for any function f. By definition, $[\hat{x}, \hat{p}_x] = -\frac{\hbar}{i}$. $\square$

Proof of (b).

$$
\begin{aligned}
[\hat{x}, \hat{p}_x^2]f &= (\hat{x}\hat{p}_x^2 - \hat{p}_x^2\hat{x})f \\
&= (\hat{x}\hat{p}_x^2)f - (\hat{p}_x^2\hat{x})f \\
&= (\hat{x}\hat{p}_x)\left(\frac{\hbar}{i}\frac{\partial f}{\partial x}\right) - (\hat{p}_x^2)(xf) \\
&= (\hat{x})\left(\frac{\hbar}{i}\frac{\hbar}{i}\frac{\partial^2 f}{\partial x^2}\right) - (\hat{p}_x)\frac{\hbar}{i}\left(f + x\frac{\partial f}{\partial x}\right) \\
&= x\left(\frac{\hbar}{i}\frac{\hbar}{i}\frac{\partial^2 f}{\partial x^2}\right) - \frac{\hbar}{i}\frac{\hbar}{i}\left(\frac{\partial f}{\partial x} + \frac{\partial f}{\partial x} + x\frac{\partial^2 f}{\partial x^2}\right) \\
&= -\frac{\hbar}{i}\frac{\hbar}{i} \cdot 2\frac{\partial f}{\partial x} \\
&= \left(2\hbar\frac{\partial}{\partial x}\right)f
\end{aligned}
$$

holds for any function f. By definition, $[\hat{x}, \hat{p}_x^2] = 2\hbar\frac{\partial}{\partial x}$. $\square$

Proof of (c).

$$
\begin{aligned}
[\hat{x}, \hat{p}_y]f &= (\hat{x}\hat{p}_y - \hat{p}_y\hat{x})f \\
&= (\hat{x}\hat{p}_y)f - (\hat{p}_y\hat{x})f \\
&= (\hat{x})\left(\frac{\hbar}{i}\frac{\partial f}{\partial y}\right) - (\hat{p}_y)(xf) \\
&= x\frac{\hbar}{i}\frac{\partial f}{\partial x} - \frac{\hbar}{i} \cdot x\frac{\partial f}{\partial y} \\
&= 0
\end{aligned}
$$

holds for any function f. By definition, $[\hat{x}, \hat{p}_y] = 0$. $\square$

Proof of (d).

$$
\begin{aligned}
[\hat{x}, \hat{V}(x,y,z)]f &= (\hat{x}\hat{V}(x,y,z) - \hat{V}(x,y,z)\hat{x})f \\
&= (\hat{x}\hat{V}(x,y,z))f - (\hat{V}(x,y,z)\hat{x})f \\
&= \hat{x}(V(x,y,z)f) - \hat{V}(x,y,z)(xf) \\
&= xV(x,y,z)f - V(x,y,z)xf \\
&= 0
\end{aligned}
$$

holds for any function f. By definition, $[\hat{x}, \hat{V}(x,y,z)] = 0$. $\square$

Proof of (e).

(1) Given any function f,

$$
\begin{aligned}
\frac{\partial^2}{\partial x^2}(fx) &= \frac{\partial}{\partial x}\left(x\frac{\partial f}{\partial x} + f\right) \\
&= \frac{\partial f}{\partial x} + x\frac{\partial^2 f}{\partial x^2} + \frac{\partial f}{\partial x} \\
&= 2\frac{\partial f}{\partial x} + x\frac{\partial^2 f}{\partial x^2}, \\
\frac{\partial^2}{\partial y^2}(fx) &= x\frac{\partial^2 f}{\partial y^2}, \\
\frac{\partial^2}{\partial z^2}(fx) &= x\frac{\partial^2 f}{\partial z^2}.
\end{aligned}
$$

(2)

$$
\begin{aligned}
(\hat{H}\hat{x})f &= (\hat{H})(xf) \\
&= -\frac{\hbar}{2m}\left(\frac{\partial^2}{\partial x^2}(xf) + \frac{\partial^2}{\partial y^2}(xf) + \frac{\partial^2}{\partial z^2}(xf)\right) + V(x,y,z)xf \\
&= -\frac{\hbar}{2m}\left(2\frac{\partial f}{\partial x} + x\frac{\partial^2 f}{\partial x^2} + x\frac{\partial^2 f}{\partial y^2} + x\frac{\partial^2 f}{\partial z^2}\right) + V(x,y,z)xf \\
&= -\frac{\hbar}{m}\frac{\partial f}{\partial x} + (\hat{x}\hat{H})f
\end{aligned}
$$

(3)

$$
\begin{aligned}
[\hat{x}, \hat{H}]f &= (\hat{x}\hat{H} - \hat{H}\hat{x})f \\
&= (\hat{x}\hat{H})f - (\hat{H}\hat{x})f \\
&= \frac{\hbar}{m}\frac{\partial f}{\partial x}
\end{aligned}
$$

holds for any function f. By definition, $[\hat{x}, \hat{H}] = \frac{\hbar}{m}\frac{\partial}{\partial x}$.

□

Proof of (f). Similar to (b), $[\hat{x}\hat{y}\hat{z}, \hat{p}_x^2] = 2\hbar yz\frac{\partial}{\partial x}$. □

Problem 3.33.

Prove the multiple-integral identity

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} F(x)G(y)H(z)dxdydz = \int_{-\infty}^{\infty} F(x)dx \int_{-\infty}^{\infty} G(y)dy \int_{-\infty}^{\infty} H(z)dz.$$

Proof. Write $\int = \int_{-\infty}^{\infty}$.

$$\begin{aligned}
&\int\int\int F(x)G(y)H(z)dxdydz \\
&= \int\int\left(\int F(x) \underbrace{G(y)H(z)}_{\text{constant w.r.t } x} dx\right) dydz \\
&= \int\int G(y)H(z) \underbrace{\int F(x)dx}_{\text{constant w.r.t } y \text{ and } z} dydz \\
&= \int F(x)dx \int\int G(y)H(z)dydz \\
&= \int F(x)dx \int G(y)dy \int H(z)dz. && \text{(Similar arguments)}
\end{aligned}$$

□