Problem 4.48

(a) Prove the **three-dimensional virial theorem**:

$$2\langle T\rangle = \langle \mathbf{r}\cdot\nabla V\rangle \tag{4.217}$$

(for stationary states). *Hint*: refer to Problem 3.37.

(b) Apply the virial theorem to the case of hydrogen, and show that

$$\langle T\rangle = -E_n; \quad \langle V\rangle = 2E_n. \tag{4.218}$$

(c) Apply the virial theorem to the three-dimensional harmonic oscillator (Problem 4.46), and show that in this case

$$\langle T\rangle = \langle V\rangle = E_n/2. \tag{4.219}$$

Solution

Part (a)

Consider the time derivative of the expectation value of $\mathbf{r}\cdot\mathbf{p}$ and use the first result of Problem 3.37.

$$\begin{aligned}
\frac{d}{dt}\langle \mathbf{r}\cdot\mathbf{p}\rangle &= \frac{d}{dt}\langle \Psi\,|\,\mathbf{r}\cdot\mathbf{p}\,|\,\Psi\rangle \\
&= \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Psi^*(x,y,z,t)(\mathbf{r}\cdot\mathbf{p})\Psi(x,y,z,t)\,dx\,dy\,dz \\
&= \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Psi^*(x,y,z,t)(xp_x+yp_y+zp_z)\Psi(x,y,z,t)\,dx\,dy\,dz \\
&= \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Psi^*(x,y,z,t)xp_x\Psi(x,y,z,t)\,dx\,dy\,dz \\
&\qquad + \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Psi^*(x,y,z,t)yp_y\Psi(x,y,z,t)\,dx\,dy\,dz \\
&\qquad\quad + \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Psi^*(x,y,z,t)zp_z\Psi(x,y,z,t)\,dx\,dy\,dz \\
&= \frac{d}{dt}\langle\Psi\,|\,xp_x\,|\,\Psi\rangle + \frac{d}{dt}\langle\Psi\,|\,yp_y\,|\,\Psi\rangle + \frac{d}{dt}\langle\Psi\,|\,zp_z\,|\,\Psi\rangle \\
&= \frac{d}{dt}\langle xp_x\rangle + \frac{d}{dt}\langle yp_y\rangle + \frac{d}{dt}\langle zp_z\rangle \\
&= \left(2\left\langle\frac{p_x^2}{2M}\right\rangle - \left\langle x\frac{\partial V}{\partial x}\right\rangle\right) + \left(2\left\langle\frac{p_y^2}{2M}\right\rangle - \left\langle y\frac{\partial V}{\partial y}\right\rangle\right) + \left(2\left\langle\frac{p_z^2}{2M}\right\rangle - \left\langle z\frac{\partial V}{\partial z}\right\rangle\right) \\
&= 2\left\langle\frac{p_x^2}{2M}+\frac{p_y^2}{2M}+\frac{p_z^2}{2M}\right\rangle - \left\langle x\frac{\partial V}{\partial x}+y\frac{\partial V}{\partial y}+z\frac{\partial V}{\partial z}\right\rangle
\end{aligned}$$

Consequently,

$$\begin{aligned}\frac{d}{dt}\langle \mathbf{r}\cdot\mathbf{p}\rangle &= 2\left\langle \frac{p_x^2+p_y^2+p_z^2}{2M}\right\rangle - \left\langle x\frac{\partial V}{\partial x}+y\frac{\partial V}{\partial y}+z\frac{\partial V}{\partial z}\right\rangle \\ &= 2\left\langle \frac{\mathbf{p}\cdot\mathbf{p}}{2M}\right\rangle - \langle \mathbf{r}\cdot\nabla V\rangle \\ &= 2\left\langle \frac{\mathbf{p}^2}{2M}\right\rangle - \langle \mathbf{r}\cdot\nabla V\rangle \\ &= 2\langle T\rangle - \langle \mathbf{r}\cdot\nabla V\rangle.\end{aligned}$$

The position-space wave function for a stationary state is of the form,

$$\Psi_{n\ell m}(x,y,z,t)=\psi_{n\ell m}(x,y,z)e^{-iE_{n\ell m}t/\hbar},$$

so this previous equation becomes

$$\begin{aligned}2\langle T\rangle - \langle \mathbf{r}\cdot\nabla V\rangle &= \frac{d}{dt}\langle \mathbf{r}\cdot\mathbf{p}\rangle \\ &= \frac{d}{dt}\langle \Psi_{n\ell m}\,|\,\mathbf{r}\cdot\mathbf{p}\,|\,\Psi_{n\ell m}\rangle \\ &= \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Psi^*_{n\ell m}(x,y,z,t)(\mathbf{r}\cdot\mathbf{p})\Psi_{n\ell m}(x,y,z,t)\,dx\,dy\,dz \\ &= \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}\right](xp_x+yp_y+zp_z)\left[\psi_{n\ell m}(x,y,z)e^{-iE_{n\ell m}t/\hbar}\right]dx\,dy\,dz \\ &= \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}\right]xp_x\left[\psi_{n\ell m}(x,y,z)e^{-iE_{n\ell m}t/\hbar}\right]dx\,dy\,dz \\ &\quad + \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}\right]yp_y\left[\psi_{n\ell m}(x,y,z)e^{-iE_{n\ell m}t/\hbar}\right]dx\,dy\,dz \\ &\quad + \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}\right]zp_z\left[\psi_{n\ell m}(x,y,z)e^{-iE_{n\ell m}t/\hbar}\right]dx\,dy\,dz \\ &= \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}\right]x\left(-i\hbar\frac{\partial}{\partial x}\right)\left[\psi_{n\ell m}(x,y,z)e^{-iE_{n\ell m}t/\hbar}\right]dx\,dy\,dz \\ &\quad + \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}\right]y\left(-i\hbar\frac{\partial}{\partial y}\right)\left[\psi_{n\ell m}(x,y,z)e^{-iE_{n\ell m}t/\hbar}\right]dx\,dy\,dz \\ &\quad + \frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}\right]z\left(-i\hbar\frac{\partial}{\partial z}\right)\left[\psi_{n\ell m}(x,y,z)e^{-iE_{n\ell m}t/\hbar}\right]dx\,dy\,dz \\ &= -i\hbar\frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}x\frac{\partial\psi_{n\ell m}}{\partial x}e^{-iE_{n\ell m}t/\hbar}\,dx\,dy\,dz \\ &\quad - i\hbar\frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}y\frac{\partial\psi_{n\ell m}}{\partial y}e^{-iE_{n\ell m}t/\hbar}\,dx\,dy\,dz \\ &\quad - i\hbar\frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*_{n\ell m}(x,y,z)e^{iE_{n\ell m}t/\hbar}z\frac{\partial\psi_{n\ell m}}{\partial z}e^{-iE_{n\ell m}t/\hbar}\,dx\,dy\,dz.\end{aligned}$$

The exponential functions cancel out, resulting in an integrand with no time dependence.

$$\begin{aligned}
2\langle T\rangle - \langle \mathbf{r}\cdot\nabla V\rangle &= -i\hbar\frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_{n\ell m}^*(x,y,z)x\frac{\partial\psi_{n\ell m}}{\partial x}\,dx\,dy\,dz \\
&\quad - i\hbar\frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_{n\ell m}^*(x,y,z)y\frac{\partial\psi_{n\ell m}}{\partial y}\,dx\,dy\,dz \\
&\quad - i\hbar\frac{d}{dt}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_{n\ell m}^*(x,y,z)z\frac{\partial\psi_{n\ell m}}{\partial z}\,dx\,dy\,dz \\
&= -i\hbar\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\partial}{\partial t}\left[\psi_{n\ell m}^*(x,y,z)x\frac{\partial\psi_{n\ell m}}{\partial x}\right]dx\,dy\,dz \\
&\quad - i\hbar\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\partial}{\partial t}\left[\psi_{n\ell m}^*(x,y,z)y\frac{\partial\psi_{n\ell m}}{\partial y}\right]dx\,dy\,dz \\
&\quad - i\hbar\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\partial}{\partial t}\left[\psi_{n\ell m}^*(x,y,z)z\frac{\partial\psi_{n\ell m}}{\partial z}\right]dx\,dy\,dz \\
&= -i\hbar\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(0)\,dx\,dy\,dz \\
&\quad - i\hbar\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(0)\,dx\,dy\,dz \\
&\quad - i\hbar\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(0)\,dx\,dy\,dz \\
&= 0
\end{aligned}$$

Therefore, for stationary states in three dimensions,

$$2\langle T\rangle = \langle \mathbf{r}\cdot\nabla V\rangle.$$

Part (b)

For the hydrogen atom, the potential energy function is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}.$$

Compute the gradient in spherical coordinates.

$$\begin{aligned}
\nabla V &= \frac{\partial V}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\underbrace{\frac{\partial V}{\partial\theta}}_{=0}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\underbrace{\frac{\partial V}{\partial\phi}}_{=0}\hat{\boldsymbol{\phi}} \\
&= \frac{d}{dr}\left(-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)\hat{\mathbf{r}} \\
&= \left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{r^2}\right)\hat{\mathbf{r}}
\end{aligned}$$

Take the dot product of the position vector with this gradient.

$$\begin{aligned}\mathbf{r}\cdot\nabla V &= (r\hat{\mathbf{r}})\cdot\left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{r^2}\hat{\mathbf{r}}\right)\\ &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}})\\ &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}(1)\\ &= \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\\ &= -V(r)\end{aligned}$$

Now apply the virial theorem for a stationary state of the hydrogen atom.

$$\begin{aligned}2\langle T\rangle &= \langle \mathbf{r}\cdot\nabla V\rangle\\ &= \langle -V(r)\rangle\\ &= -\langle V\rangle \qquad (1)\end{aligned}$$

The Hamiltonian is the sum of the kinetic energy and the potential energy,

$$H = T + V,$$

and its expectation value is the energy of the state.

$$\begin{aligned}\langle H\rangle &= \langle T + V\rangle\\ E_n &= \langle T\rangle + \langle V\rangle \qquad (2)\end{aligned}$$

Equations (1) and (2) form a system of two equations with two unknowns that can be solved.

$$\begin{cases}\langle T\rangle + \langle V\rangle = E_n\\ 2\langle T\rangle + \langle V\rangle = 0\end{cases}$$

Solving it yields

$$\langle T\rangle = -E_n \quad \text{and} \quad \langle V\rangle = 2E_n.$$

Part (c)

For the three-dimensional harmonic oscillator, the potential energy function is

$$V(r) = \frac{1}{2}M\omega^2 r^2.$$

Compute the gradient in spherical coordinates.

$$\begin{aligned}\nabla V &= \frac{\partial V}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\underbrace{\frac{\partial V}{\partial \theta}}_{=0}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\underbrace{\frac{\partial V}{\partial \phi}}_{=0}\hat{\boldsymbol{\phi}}\\ &= \frac{d}{dr}\left(\frac{1}{2}M\omega^2 r^2\right)\hat{\mathbf{r}}\\ &= M\omega^2 r\hat{\mathbf{r}}\end{aligned}$$

Take the dot product of the position vector with this gradient.

$$\begin{aligned}\mathbf{r}\cdot\nabla V &= (r\hat{\mathbf{r}})\cdot(M\omega^2 r\hat{\mathbf{r}})\\ &= M\omega^2 r^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}})\\ &= M\omega^2 r^2(1)\\ &= M\omega^2 r^2\\ &= 2V(r)\end{aligned}$$

Now apply the virial theorem for a stationary state of the harmonic oscillator.

$$\begin{aligned}2\langle T\rangle &= \langle \mathbf{r}\cdot\nabla V\rangle\\ &= \langle 2V(r)\rangle\\ &= 2\langle V\rangle \qquad (3)\end{aligned}$$

The Hamiltonian is the sum of the kinetic energy and the potential energy,

$$H = T + V,$$

and its expectation value is the energy of the state.

$$\begin{aligned}\langle H\rangle &= \langle T + V\rangle\\ E_n &= \langle T\rangle + \langle V\rangle \qquad (4)\end{aligned}$$

Equations (3) and (4) form a system of two equations with two unknowns that can be solved.

$$\begin{cases}\langle T\rangle + \langle V\rangle = E_n\\ \langle T\rangle - \langle V\rangle = 0\end{cases}$$

Solving it yields

$$\langle T\rangle = \frac{1}{2}E_n \quad \text{and} \quad \langle V\rangle = \frac{1}{2}E_n.$$