Solutions 3

Harmonic oscillator problems are simplified by noting that the energy eigenfunctions are functions only of $y = x/\alpha$. Treating the eigenfunctions as functions of y rather than x, leads to a scaled Hamiltonian, and associated energy eigenstates and raising and lowering operators.

$$\hat{H} = \frac{1}{2}\left(-\frac{d^2}{dy^2} + y^2\right) = \hat{a}^\dagger\hat{a} + \frac{1}{2},$$

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\frac{d}{dy} + y\right),$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}}\left(-\frac{d}{dy} + y\right),$$

$$\psi_0(y) = \pi^{-1/2}\exp\left(-\frac{y^2}{2}\right),$$

$$\psi_{\upsilon+1}(y) = \frac{1}{\sqrt{\upsilon+1}}\hat{a}^\dagger\psi_\upsilon(y)$$

and

$$\psi_{\upsilon-1}(y) = \frac{1}{\sqrt{\upsilon}}\hat{a}\psi_\upsilon(y)$$

The (scaled) energy eigenvalues are made explicit in the following TISE:

$$\hat{H}\psi_\upsilon(y) = \left(\upsilon + \frac{1}{2}\right)\psi_\upsilon(y).$$

1. Determine the first and second excited states, $\psi_1(y)$ and $\psi_2(y)$, from the ground state, $\psi_0(y)$, using the raising operator, $\hat{a}^\dagger$.

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The first excited state is given by

$$\begin{aligned}
\psi_1(y) &= \frac{1}{\sqrt{1}}\hat{a}^\dagger\psi_0(y) \\
&= \frac{1}{\sqrt{2}}\left(-\frac{d}{dy} + y\right)\pi^{1/2}\exp\left(-\frac{y^2}{2}\right) \\
&= \left(\frac{\pi}{2}\right)^{1/2}\left(-\frac{d}{dy} + y\right)\exp\left(-\frac{y^2}{2}\right) \\
&= \left(\frac{\pi}{2}\right)^{1/2} 2y\exp\left(-\frac{y^2}{2}\right) \\
&= \left(\frac{\pi}{2}\right)^{1/2} H_1(y)\exp\left(-\frac{y^2}{2}\right)
\end{aligned}$$

The Hermite polynomial, $H_1(y) = 2y$. The second excited state is given by

$$\begin{aligned}
\psi_2(y) &= \frac{1}{\sqrt{2}}\hat{a}^\dagger \psi_1(y) \\
&= \frac{1}{2}\left(-\frac{d}{dy} + y\right)\left(\frac{\pi}{2}\right)^{1/2} 2y \exp\left(-\frac{y^2}{2}\right) \\
&= \frac{1}{2}\left(\frac{\pi}{2}\right)^{1/2}(-2 + 2y^2 + 2y^2)\exp\left(-\frac{y^2}{2}\right) \\
&= \frac{1}{2}\left(\frac{\pi}{2}\right)^{1/2}(4y^2 - 2)\exp\left(-\frac{y^2}{2}\right) \\
&= \frac{1}{2}\left(\frac{\pi}{2}\right)^{1/2} H_2(y)\exp\left(-\frac{y^2}{2}\right)
\end{aligned}$$

The Hermite polynomial, $H_2(y) = 4y^2 - 2$.

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2. Determine the uncertainty in position, y, and associated momentum, $\hat{p} = -i\hbar d/dy$, for the υ th excited state of the harmonic oscillator. Show that they satisfy the uncertainty principle.

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We need the expectation values of y, y^2, $\hat{p}$ and $\hat{p}^2$. First write y and $\hat{p}$ in terms of raising and lowering operators,

$$y = \frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger)$$

and

$$\hat{p} = -i\hbar\frac{d}{dy} = \frac{-i\hbar}{\sqrt{2}}(\hat{a} - \hat{a}^\dagger).$$

Since $y\psi_\upsilon(y)$ is a linear combination of $\psi_{\upsilon+1}(y)$ and $\psi_{\upsilon-1}(y)$ (unless $\upsilon = 0$), the inner product of $\psi_\upsilon(y)$ with $y\psi_\upsilon(y)$ (i.e., the expectation of y in state, $\psi_\upsilon(y)$) is zero - ψ_υ is orthogonal to $\psi_{\upsilon+1}$ and $\psi_{\upsilon-1}$. Specifically,

$$\begin{aligned}
\langle\psi_\upsilon|y\psi_\upsilon\rangle &= \left\langle\psi_\upsilon\left|\frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger)\psi_\upsilon\right.\right\rangle \\
&= \frac{1}{\sqrt{2}}\langle\psi_\upsilon|(\hat{a}\psi_\upsilon + \hat{a}^\dagger\psi_\upsilon)\rangle \\
&= \frac{1}{\sqrt{2}}\left\langle\psi_\upsilon\left|\left(\sqrt{\upsilon}\,\psi_{\upsilon-1} + \sqrt{\upsilon+1}\,\psi_{\upsilon+1}\right)\right.\right\rangle \\
&= \frac{1}{\sqrt{2}}\left(\sqrt{\upsilon}\,\langle\psi_\upsilon|\psi_{\upsilon-1}\rangle + \sqrt{\upsilon+1}\,\langle\psi_\upsilon|\psi_{\upsilon+1}\rangle\right) \\
&= 0.
\end{aligned}$$

Similarly, $\langle\psi_\upsilon|\hat{p}\psi_\upsilon\rangle = 0$. The expectations of y^2 and $\hat{p}^2$ are given by

$$
\begin{aligned}
\langle\psi_\upsilon|y^2\psi_\upsilon\rangle &= \left\langle\psi_\upsilon\left|\frac{1}{\sqrt{2}}(\hat{a}+\hat{a}^\dagger)\frac{1}{\sqrt{2}}(\hat{a}+\hat{a}^\dagger)\psi_\upsilon\right.\right\rangle \\
&= \frac{1}{2}\langle\psi_\upsilon|(\hat{a}+\hat{a}^\dagger)(\hat{a}\psi_\upsilon+\hat{a}^\dagger\psi_\upsilon)\rangle \\
&= \frac{1}{2}\left\langle\psi_\upsilon\left|\left(\sqrt{\upsilon}\,(\hat{a}+\hat{a}^\dagger)\psi_{\upsilon-1}+\sqrt{\upsilon+1}\,(\hat{a}+\hat{a}^\dagger)\psi_{\upsilon+1}\right)\right.\right\rangle \\
&= \frac{1}{2}\left(\sqrt{\upsilon(\upsilon-1)}\,\langle\psi_\upsilon|\psi_{\upsilon-2}\rangle+\upsilon\langle\psi_\upsilon|\psi_\upsilon\rangle+(\upsilon+1)\langle\psi_\upsilon|\psi_\upsilon\rangle+\sqrt{(\upsilon+1)(\upsilon+2)}\,\langle\psi_\upsilon|\psi_{\upsilon+2}\rangle\right) \\
&= \left(\upsilon+\frac{1}{2}\right)\langle\psi_\upsilon|\psi_\upsilon\rangle = \upsilon+\frac{1}{2}.
\end{aligned}
$$

and

$$
\begin{aligned}
\langle\psi_\upsilon|\hat{p}^2\psi_\upsilon\rangle &= \left\langle\psi_\upsilon\left|\frac{(-i\hbar)}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)\frac{(-i\hbar)}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)\psi_\upsilon\right.\right\rangle \\
&= \frac{-\hbar^2}{2}\langle\psi_\upsilon|(\hat{a}-\hat{a}^\dagger)(\hat{a}\psi_\upsilon-\hat{a}^\dagger\psi_\upsilon)\rangle \\
&= \frac{-\hbar^2}{2}\left\langle\psi_\upsilon\left|\left(\sqrt{\upsilon}\,(\hat{a}-\hat{a}^\dagger)\psi_{\upsilon-1}-\sqrt{\upsilon+1}\,(\hat{a}-\hat{a}^\dagger)\psi_{\upsilon+1}\right)\right.\right\rangle \\
&= \frac{-\hbar^2}{2}\left(\sqrt{\upsilon(\upsilon-1)}\,\langle\psi_\upsilon|\psi_{\upsilon-2}\rangle-\upsilon\langle\psi_\upsilon|\psi_\upsilon\rangle-(\upsilon+1)\langle\psi_\upsilon|\psi_\upsilon\rangle+\sqrt{(\upsilon+1)(\upsilon+2)}\,\langle\psi_\upsilon|\psi_{\upsilon+2}\rangle\right) \\
&= \hbar^2\left(\upsilon+\frac{1}{2}\right)\langle\psi_\upsilon|\psi_\upsilon\rangle = \hbar^2\left(\upsilon+\frac{1}{2}\right).
\end{aligned}
$$

Finally, we have the uncertainties

$$
\begin{aligned}
\sigma_y &= \left(\langle\psi_\upsilon|y^2\psi_\upsilon\rangle-\langle\psi_\upsilon|y\psi_\upsilon\rangle^2\right)^{1/2} \\
&= \left(\upsilon+\frac{1}{2}\right)^{1/2}
\end{aligned}
$$

and

$$
\begin{aligned}
\sigma_p &= \left(\langle\psi_\upsilon|\hat{p}^2\psi_\upsilon\rangle-\langle\psi_\upsilon|\hat{p}\psi_\upsilon\rangle^2\right)^{1/2} \\
&= \hbar\left(\upsilon+\frac{1}{2}\right)^{1/2},
\end{aligned}
$$

and the product of uncertainties,

$$
\sigma_y\sigma_p = \left(\upsilon+\frac{1}{2}\right)\hbar \geq \frac{\hbar}{2},
$$

in accord with the uncertainty principle.

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3. Determine the transition matrix element,

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\langle\psi_{\upsilon+1}|y\psi_\upsilon\rangle
$$

for the dipole transition from the υ th to $\upsilon+1$ th state.

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$$
\begin{aligned}
\langle \psi_{\upsilon+1} | y \psi_\upsilon \rangle &= \left\langle \psi_{\upsilon+1} \middle| \frac{1}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger) \psi_\upsilon \right\rangle \\
&= \frac{1}{\sqrt{2}} \left\langle \psi_{\upsilon+1} \middle| \left(\sqrt{\upsilon}\, \psi_{\upsilon-1} + \sqrt{\upsilon+1}\, \psi_{\upsilon+1} \right) \right\rangle \\
&= \frac{1}{\sqrt{2}} \left(\sqrt{\upsilon} \langle \psi_{\upsilon+1} | \psi_{\upsilon-1} \rangle + \sqrt{\upsilon+1} \langle \psi_{\upsilon+1} | \psi_{\upsilon+1} \rangle \right) \\
&= \sqrt{\frac{\upsilon+1}{2}} \neq 0.
\end{aligned}
$$

This means that transitions between successive energy levels of a harmonic oscillator are dipole allowed. Dipole allowed means that transitions can occur with low intensity incident light. High intensity light is required to cause higher order transitions governed by transition matrix elements of y^2, y^3 etc..

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4. Determine the transition matrix element,

$$\langle \psi_{\upsilon+2} | y \psi_\upsilon \rangle$$

for the dipole transition from the υ th to $\upsilon + 2$ th state.

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This calculation is almost identical to the previous calculation - only $\psi_{\upsilon+1}$ is replaced by $\psi_{\upsilon+2}$.

$$
\begin{aligned}
\langle \psi_{\upsilon+2} | y \psi_\upsilon \rangle &= \left\langle \psi_{\upsilon+2} \middle| \frac{1}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger) \psi_\upsilon \right\rangle \\
&= \frac{1}{\sqrt{2}} \left\langle \psi_{\upsilon+2} \middle| \left(\sqrt{\upsilon}\, \psi_{\upsilon-1} + \sqrt{\upsilon+1}\, \psi_{\upsilon+1} \right) \right\rangle \\
&= \frac{1}{\sqrt{2}} \left(\sqrt{\upsilon} \langle \psi_{\upsilon+2} | \psi_{\upsilon-1} \rangle + \sqrt{\upsilon+1} \langle \psi_{\upsilon+2} | \psi_{\upsilon+1} \rangle \right) \\
&= 0.
\end{aligned}
$$

$\Delta\upsilon = \pm 2$ transitions are not dipole allowed for harmonic oscillators. In the specta of real molecules, such transitions can be observed. However, they are weak. These overtone transitions appear because of anharmonicity - the real interatomic potential is only close to parabolic close to the equilibrium bond distance. The true energy eigenstates are perturbed harmonic oscillator eigenstates - i.e., they are distorted somewhat away from the harmonic oscillator states.

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