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Harmonic oscillator states & expectation values of operators

Harmonic oscillator solutions

The wave functions for the harmonic oscillator are given by:

$\psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$ with $\alpha = \frac{2\pi \nu m}{\hbar}$ and normalization constant, $N_v = (\frac{\alpha}{\pi})^{1/4}\frac{1}{2^v v!}$

and the corresponding energy eigenvalues are

$E_v = (v+\frac{1}{2})h\nu$ with $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$

The functions $H_v(\alpha^{1/2}x)$--or $H_v(z)$ if we let $z = \alpha^{1/2}x$--are a set of orthogonal polynomials on $(-\infty,\infty)$ with a Gaussian weight function. These polynomials are called the Hermite polynomials:

v	$H_v(z)$
0	1
1	$2z$
2	$4z^2 - 2$
3	$8z^3 - 12z$
4	$16z^4 - 48z^2 + 12$
5	$32z^5 - 160z^3 + 120z$
6	$64z^6 - 480z^4 + 720z^2 - 120$
.	.

In order to obtain higher degree polynomials one can use the recursion formula:

$$H_{v+1} = 2zH_v - 2vH_{v-1}$$

Expectation values

It is easy to see that the expectation value of any *odd* function like x, x^3, etc. will be zero:

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi_v^*(x)x\psi_v(x)dx = \int_{-\infty}^{+\infty} x\psi_v^*(x)\psi_v(x)dx = \int_{-\infty}^{+\infty} x|\psi_v(x)|^2dx$$

Whether ψ is even or odd, $|\psi|^2$ is always even, so the integral of an odd power of x with the 'square' of the wave function will always be zero (over symmetric limits).

Now let us look at the expectation value of an even power, like x^2 in the state ψ_0

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} \psi_0^*(x)x^2\psi_0(x)dx = \int_{-\infty}^{+\infty} N_0xH_0(z)e^{-z^2/2}N_0xH_0(z)e^{-z^2/2}dx$$

here we have inserted the definition of ψ_0 and then rearranged the order of operators, xx, since they act just by simple multiplication.

Note now that

$$xH_0 = \alpha^{-1/2} z H_0 = \frac{1}{2}\alpha^{-1/2} H_1$$

so the above expression becomes

$$\langle x^2\rangle = \int_{-\infty}^{+\infty} N_0 \frac{\alpha^{-1/2}}{2} H_1(z) e^{-z^2/2} N_0 \frac{\alpha^{-1/2}}{2} H_1(z) e^{-z^2/2} dx = \frac{N_0^2}{N_1^2} \frac{1}{4\alpha} \int_{-\infty}^{+\infty} N_1 H_1(z) e^{-z^2/2} N_1 H_1(z) e^{-z^2/2} dx$$

this last integral is just the normalization integral for $\psi_1(x)$ and has the value unity so,

$$\langle x^2\rangle = \frac{N_0^2}{N_1^2 4\alpha} = \frac{(\frac{\alpha}{\pi})^{1/2} \frac{1}{2^0 0!}}{(\frac{\alpha}{\pi})^{1/2} \frac{1}{2^1 1!} 4\alpha}$$

$$\mathbf{\langle x^2\rangle = \frac{1}{2\alpha}} = \frac{\hbar}{2\sqrt{mk}}$$

Let's now see how to deal with the momentum operator $p = -i\hbar \frac{\partial}{\partial x}$. Can we think of p as even or odd? Can we move p around in the integrand like we did x? Consider operating with p on ψ_0:

$$-ih\frac{\partial}{\partial x}\ \psi_0(x) = -i\hbar \frac{\partial}{\partial x}\ N_0 H_0(z) e^{-z^2/2} = -i\hbar N_0 \frac{\partial}{\partial x}\ e^{-\alpha x^2/2} = -i\hbar N_0 \frac{-2\alpha x}{2}\ e^{-\alpha x^2/2}$$

$$= \frac{i\hbar N_0 \alpha^{1/2}}{2} 2\alpha^{1/2} x e^{-\alpha x^2/2} = \frac{i\hbar N_0 \alpha^{1/2}}{2} 2z e^{-\alpha x^2/2} = \frac{i\hbar N_0 \alpha^{1/2}}{2} H_1 e^{-z^2/2}$$

$$= \frac{i\hbar N_0 \alpha^{1/2}}{2N_1} N_1 H_1 e^{-z^2/2} = \frac{i\hbar N_0 \alpha^{1/2}}{2N_1} \psi_1$$

We can now use this result to evalute <p>:

$$\mathbf{\langle p\rangle} = \int_{-\infty}^{+\infty} \psi_0^*(x) \left[-i\hbar \frac{\partial}{\partial x}\right] \psi_0(x) dx = \int_{-\infty}^{+\infty} \psi_0^*(x) \frac{i\hbar N_0 \alpha^{1/2}}{2N_1} \psi_1(x) dx$$

$\mathbf{\langle p\rangle = 0}$ since ψ_0 and ψ_1 are orthogonal.

What about $\langle p^2\rangle$? Let's apply the derivative operator twice to ψ_0. Recall that

$$-i\hbar \frac{\partial}{\partial x} \psi_0(x) = -i\hbar N_0 \frac{-2\alpha x}{2}\ e^{-\alpha x^2/2} \text{ so}$$

$$-i\hbar \frac{\partial}{\partial x}\left[-i\hbar \frac{\partial}{\partial x}\psi_0(x)\right] = -i\hbar \frac{\partial}{\partial x}\left(-i\hbar N_0 \frac{-2\alpha x}{2} e^{-\alpha x^2/2}\right) = -\hbar^2 N_0 \frac{\partial}{\partial x}\frac{-2\alpha x}{2} e^{-\alpha x^2/2}$$

$$= -\hbar^2 N_0\left[\frac{-2\alpha}{2} + \frac{-2\alpha x}{2}\frac{-2\alpha x}{2}\right]e^{-\alpha x^2/2}$$

$$= -\hbar^2 N_0\left[\alpha^2 x^2 - \alpha\right]e^{-\alpha x^2/2}$$

where we have used the product rule.

We now rearrange all this in terms of $z=\alpha^{1/2}x$:

$$p^2\psi_0 = -\hbar^2 N_0\alpha\left[z^2 - 1\right]e^{-z^2/2} = \frac{-\hbar^2 N_0\alpha}{4}\left[4z^2 - 4\right]e^{-z^2/2} = \frac{-\hbar^2 N_0\alpha}{4}\left[4z^2 - 2 - 2\right]e^{-z^2/2}$$

$$= \frac{-\hbar^2 N_0\alpha}{4}\left[H_2 - 2H_0\right]e^{-z^2/2} = \frac{-h^2 N_0\alpha}{4}\left[\frac{N_2}{N_2}H_2 - 2\frac{N_0}{N_0}H_0\right]e^{-z^2/2}$$

$$= \frac{-\hbar^2 N_0\alpha}{4}\left[\frac{\psi_2}{N_2} - 2\frac{\psi_0}{N_0}\right].$$

We now use this to get the expectation value of p^2:

$$\langle p^2\rangle = \int_{-\infty}^{+\infty}\psi_0^* p^2\psi_0\,dx = \frac{-\hbar^2 N_0\alpha}{4}\int_{-\infty}^{+\infty}\psi_{0^*}\left[\frac{\psi_2}{N_2} - 2\frac{\psi_0}{N_0}\right]dx$$

$$= \frac{-\hbar^2 N_0\alpha}{4}\left[\frac{1}{N_2}\int_{-\infty}^{+\infty}\psi_0^*\psi_2\,dx - \frac{2}{N_0}\int_{-\infty}^{+\infty}\psi_0^*\psi_0\,dx\right]$$

Since the first integral in the bracket is zero and the second is unity, we get:

$$\boldsymbol{\langle p^2\rangle} = \frac{\hbar^2 N_0\alpha}{4}\frac{2}{N_0} = \frac{\hbar^2\alpha}{\mathbf{2}}$$

How do we generalize this? What about $\langle p^3\rangle$? We saw that p acting on ψ_0 yielded ψ_1 while p^2 acting on ψ_0 yielded a combination of ψ_2 and ψ_0. We can generalize and say that if n is odd, p^n will change an even function to a combination of odd functions and will change an odd function to a combination of even functions. If n is even, p^n will change an even function to a combination of even functions and so forth.

The power of the Hermite polynomials is that any series of terms like

$$c_0 + c_1 y + c_2 y^2 + \cdots$$

can be written in terms of the set of orthogonal polynomials and the integrals reduced to a sum of terms containing integrals which are zero or one ($\delta_{v'v}$).

Why are we interested in expectation values of x or sandwiching x between wavefunctions and integrating? One answer is that the observable corresponding to the dipole operator is qx where q is a charge. When a light wave passes by a molecule, the electric vector of the wave interacts with the dipole moment of the molecule. This is the "hook" that allows molecules to absorb radiation and to be excited to upper states. The intensity of the absorption for a molecule starting in ψ_0 and being excited by the appropriate frequency light ($\nu = (E_1 - E_0)/h$ to ψ_1 is proportional to the integral:

$$\int_{-\infty}^{+\infty} \psi_1^* x \psi_0 dx \ .$$

For applications to the infrared spectroscopy of molecular vibrations, harmonic oscillator states are a good approximation to these wavefunctions.