Harmonic Oscillator with a cubic perturbation

Background

The harmonic oscillator is ubiquitous in theoretical chemistry and is the model used for most vibrational spectroscopy. A particle is a harmonic oscillator if it experiences a force that is always directed toward a point (the origin) and which varies linearly with the distance from the origin. In one dimension this means $\boldsymbol{F} = -kx\hat{x}$ where k is the force constant. This force in turn corresponds to the potential energy $V = \frac{1}{2}kx^2$ and so the Hamiltonian for the HO is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

The Schrodinger equation $\hat{H}\Phi = E\Phi$ has the eigenvalues $E_n = (n + \frac{1}{2})h\nu$ where $n = 0,1,2,\cdots$ and $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$. The eigenfunctions are

$\Phi_n(x) = N_n H_n(\alpha^{1/2}x)e^{-\alpha x^2}$ where $\alpha = \left(\frac{km}{\hbar^2}\right)^{1/2}$ N_n is a normalization constant and H_n is a Hermite polynomial, the first few being:

$$H_0(\xi) = 1 \qquad H_1(\xi) = 2\xi$$
$$H_2(\xi) = 4\xi^2 - 2 \qquad H_3(\xi) = 8\xi^3 - 12\xi$$
$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \qquad H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$$

The first four eigenfunctions are

$$\Phi_0(x) = \left(\alpha/\pi\right)^{1/4} e^{-\alpha x^2/2} \qquad \Phi_2(x) = \left(\alpha/4\pi\right)^{1/4}\left(2\alpha x^2 - 1\right)e^{-\alpha x^2/2}$$
$$\Phi_1(x) = \left(4\alpha^3/\pi\right)^{1/4} xe^{-\alpha x^2/2} \qquad \Phi_3(x) = \left(\alpha^3/9\pi\right)^{1/4}\left(2\alpha x^3 - 3x\right)e^{-\alpha x^2/2}$$

Cubic Perturbation

Suppose we are interested in estimating the eigenvalues and eigenvectors associated with the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \lambda x^3 = \hat{H}^0 + \lambda x^3$$

The first order correction to the energy of the state Φ_n^0 is then zero by parity arguments.

$$E_n^{(1)} = \left\langle \Phi_n^0 \middle| \lambda x^3 \middle| \Phi_n^0 \right\rangle = 0$$

The second order correction is

$$E_n^{(2)} = \sum_{p \neq n} \frac{\left| \left\langle \Phi_n^0 \middle| \hat{V} \middle| \Phi_p^0 \right\rangle \right|^2}{E_n^0 - E_p^0} = \sum_{p \neq n} \frac{\left| \left\langle \Phi_n^0 \middle| \lambda x^3 \middle| \Phi_p^0 \right\rangle \right|^2}{h\nu(n-p)} = \sum_{p \neq n} \frac{\left| \left\langle n \middle| \lambda x^3 \middle| p \right\rangle \right|^2}{h\nu(n-p)}$$

So we need to evaluate matrix elements of x^3 between various harmonic oscillator states. Using recursion relationships between the Hermite polynomials many texts show that

$$\langle i | x | j \rangle = \delta_{j,i-1} \sqrt{\frac{j+1}{2\alpha}} + \delta_{j,i+1} \sqrt{\frac{j}{2\alpha}} = (x)_{ij}$$

This result allows us to evaluate matrix elements of x^l for any positive integer value of l using the resolution of the identity. Since the set of eigenfunctions Φ_n^0 is complete we may write

$$\hat{1} = \sum_{n=0}^{\infty} \left| \Phi_n^0 \right\rangle \left\langle \Phi_n^0 \right| = \sum_{n=0}^{\infty} | n \rangle \langle n |$$

So

$\langle i | x^2 | j \rangle = (x^2)_{ij} = \langle i | xx | j \rangle = \sum_{n=0}^{\infty} \langle i | x | n \rangle \langle n | x | j \rangle$ or in a more explicit matrix form

$$(x^2)_{ij} = \sum_{n=0}^{\infty} (x)_{in} (x)_{nj}$$

Using the above result for $(x)_{ij}$ the sum can be evaluated and we obtain

$$(x^2)_{ij} = \sqrt{\frac{i(i+1)}{4\alpha^2}} \delta_{j,i-2} + \frac{2i+1}{2\alpha} \delta_{ij} + \sqrt{\frac{(i+1)(i+2)}{4\alpha^2}} \delta_{j,i+2}$$

Note the systematics. The matrix element $(x)_{ij}$ is zero unless i & j differ by 1, say j is equal to $i+1 \,\&\, i-1$. The matrix element $(x^2)_{ij}$ is zero unless j equals $i-2, i, i+2$. The matrix element $(x^3)_{ij}$ will vanish unless $j = i+3, i+1, i-1 \,\&\, i-3$ whereas $(x^4)_{ij}$ will vanish except for $j = i+4, i+2, i, i-2, i-4$, and so on. Returning to the perturbation sum for $E_n^{(2)}$ we see

$$E_n^{(2)} = \frac{\lambda^2}{h\nu}\sum_{p\neq n}\frac{(x^3)_{np}^2}{(n-p)} = \frac{\lambda^2}{h\nu}\left(\frac{(x^3)_{n,n+3}^2}{-3} + \frac{(x^3)_{n,n+1}^2}{-1} + \frac{(x^3)_{n,n-1}^2}{1}\frac{(x^3)_{n,n-3}^2}{3}\right)$$

Now $\quad (x^3)_{n,n+3} = \sum_{k=0}^{\infty}(x^2)_{n,k}(x)_{k,n+3}$

and since $(x)_{k,n+3}$ vanishes unless $k = n+2$ *or n+4* we have

$$(x^3)_{n,n+3} = (x^2)_{n,n+4}(x)_{n+4,n+3} + (x^2)_{n,n+2}(x)_{n+2,n+3}$$

and since $(x^2)_{n,n+4} = 0$, we have

$$(x^3)_{n,n+3} = (x^2)_{n,n+2}(x)_{n+2,n+3} = \sqrt{\frac{(n+2)(n+1)(n+3)}{(2\alpha)^3}}$$

In a similar fashion we find

$$(x^3)_{n,n+1} = 3\sqrt{\frac{(n+1)^3}{(2\alpha)^3}}$$

$$(x^3)_{n,n-1} = 3\sqrt{\frac{n^3}{(2\alpha)^3}}$$

$$(x^3)_{n,n-3} = \sqrt{\frac{n(n-1)n-2)}{(2\alpha)^3}}$$

Assembling these components we find

$$E_n^{(2)} = -\frac{30\lambda^2}{h\nu(2\alpha)^3}(n^2+n+11/30)$$

The first order correction to the wavefunction depends on the same matrix elements so

$$\Phi_n^{(1)} = \frac{\lambda}{h\nu}\sum_{p\neq n}\frac{(x^3)_{np}\Phi_p^0}{(n-p)} = \frac{\lambda}{h\nu}\left(\frac{(x^3)_{n,n+3}\Phi_{n+3}^0}{-3} + \frac{(x^3)_{n,n+1}\Phi_{n+1}^0}{-1} + \frac{(x^3)_{n,n-1}\Phi_{n-1}^0}{1} + \frac{(x^3)_{n,n-3}\Phi_{n-3}^0}{3}\right)$$