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# Quantum Harmonic Oscillator Eigenvalues and Wavefunctions:

Short derivation using computer algebra package *Mathematica*

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- This notebook illustrates the ability of *Mathematica* to facilitate conceptual analysis of mathematically difficult problems.

Quantum harmonic oscillator is an important model system taught in upper level physics and physical chemistry courses. In chemistry, quantum harmonic oscillator is often used to as a simple, analytically solvable model of a vibrating diatomic molecule. The model captures well the essence of harmonically vibrating bonds, and serves as a starting point for more accurate treatments of anharmonic vibrations in molecules.

The classical harmonic oscillator is a system of two masses that vibrate in quadratic potential well ( $v = \frac{k}{2} x^2$ ) without friction. The system can be characterized by its harmonic vibrational frequency  $\nu$ , force constant  $k$  (the second derivative of energy with respect to distance), and the reduced mass  $\mu$ . These three characteristics are related to each other; the frequency depends on the force constant (oscillators with stiff bonds have high frequencies) and the reduced mass (oscillators with larger reduced masses vibrate at lower frequencies). The classical frequency

is given as  $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$

Our first goal is to solve the Schrödinger equation for quantum harmonic oscillator and find out how the energy levels are related to the harmonic frequency. Thus, we need to rewrite the harmonic potential in terms of the frequency and the reduced mass.

```
In[2]:= Remove["Global`*"]
```

```
In[3]:= (* Express the force constant in terms of the reduced mass and harmonic frequency *)
```

```
kharm = Solve[v ==  $\frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ , k] // Flatten
```

```
Out[3]= {k -> 4  $\pi^2 \mu \nu^2$ }
```

```
In[4]:= (* Classical harmonic potential for the harmonic oscillator in terms of the force constant k is: *)
```

```
Vquad =  $\frac{k}{2} x^2$  ;
```

```
In[5]:= (* Classical harmonic potential for the harmonic oscillator in terms of the reduced mass and frequency is: *)
```

```
Vho = Vquad /. kharm
```

```
Out[5]= 2  $\pi^2 x^2 \mu \nu^2$ 
```

- The Schrödinger equation contains the Hamiltonian, which is a sum of the quantum mechanical kinetic energy operator and the quantum mechanical potential energy operator. The quantum mechanical kinetic energy operator in one dimension can be easily derived from the quantum

mechanical momentum operator ( $\hat{p} = -i \frac{\hbar}{2\pi} \frac{\partial}{\partial x}$ ) by recalling that the relationship between the kinetic energy and the momentum is:  $E_{\text{kin}} = \frac{\mu \vec{v}^2}{2} = \frac{\vec{p}^2}{2\mu}$ . In the case of harmonic oscillator, the action of a quantum mechanical potential operator is identical to the multiplication with the classical potential.

```
In[6]:= (* Hamiltonian for the Quantum Harmonic Oscillator:  $\hat{H} = \hat{H}_{\text{kin}} + \hat{H}_{\text{pot}}$  *)
```

$$H[f_] = -\frac{\hbar^2}{8\mu\pi^2} \text{Dt}[f, \{x, 2\}] + Vho * f$$

$$\text{Out[6]} = 2 f \pi^2 x^2 \mu v^2 - \frac{\hbar^2 \text{Dt}[f, \{x, 2\}]}{8 \pi^2 \mu}$$

```
In[7]:= (* Solving the Vibrational Schrödinger Equation:  $\hat{H} \Psi = E \Psi$  *)
```

```
VibrWF = DSolve[H[Ψ[x]] == Energy[v] * Ψ[x], Ψ[x], x]
```

$$\text{Out[7]} = \left\{ \left\{ \Psi[x] \rightarrow C[2] \text{ParabolicCylinderD}\left[\frac{-\hbar v - 2 \text{Energy}[v]}{2 \hbar v}, \frac{2 i \sqrt{2} \pi x \sqrt{\mu} \sqrt{v}}{\sqrt{\hbar}}\right] \right\} + \right. \\ \left. C[1] \text{ParabolicCylinderD}\left[\frac{-\hbar v + 2 \text{Energy}[v]}{2 \hbar v}, \frac{2 \sqrt{2} \pi x \sqrt{\mu} \sqrt{v}}{\sqrt{\hbar}}\right] \right\}$$

```
In[8]:= (* Consider solutions with real variables only *)
```

```
solnHerm = FunctionExpand[Ψ[x] /. VibrWF] /. C[2] → 0
```

$$\text{Out[8]} = \left\{ 2^{-\frac{\hbar v + 2 \text{Energy}[v]}{4 \hbar v}} e^{-\frac{2 \pi^2 x^2 \mu v}{\hbar}} C[1] \text{HermiteH}\left[\frac{-\hbar v + 2 \text{Energy}[v]}{2 \hbar v}, \frac{2 \pi x \sqrt{\mu} \sqrt{v}}{\sqrt{\hbar}}\right] \right\}$$

```
In[9]:= (* Obtain allowed energies by restricting Hermite polynomials to integer orders *)
```

$$\text{En}[v_] = \text{Solve}\left[\frac{2 \text{Energy}[v] - \hbar v}{2 \hbar v} == 0 + v, \text{Energy}[v]\right]$$

```
EnHO = Table[Energy[v] /. En[v], {v, 0, 2}] // Flatten
```

$$\text{Out[9]} = \left\{ \left\{ \text{Energy}[v] \rightarrow \frac{1}{2} \hbar (1 + 2 v) v \right\} \right\}$$

$$\text{Out[10]} = \left\{ \frac{\hbar v}{2}, \frac{3 \hbar v}{2}, \frac{5 \hbar v}{2} \right\}$$

- We see that the concept of quantized vibrational energy states ( $v = 0, 1, 2, 3 \dots$ ) arises naturally from the discrete spectrum of physically realistic eigenvalues of the solution to the vibrational Schrödinger equation. This spectrum can be experimentally probed using infrared spectroscopy.

```
In[11]:= (* General vibrational wavefunction *)
```

```
Ψ[v_, x_] = Simplify[solnHerm /. En[v]] // Flatten
```

$$\text{Out[11]} = \left\{ 2^{-v/2} e^{-\frac{2 \pi^2 x^2 \mu v}{\hbar}} C[1] \text{HermiteH}\left[v, \frac{2 \pi x \sqrt{\mu} \sqrt{v}}{\sqrt{\hbar}}\right] \right\}$$

Cell[TextData[{Cell[TextData[{ValueBox["FileName"]}], "Header"], Cell[" ", "Header", CellFrame -> {{0, 0.5}, {0, 0}}, CellFrameMargins -> 4], " ", Cell[TextData[{CounterBox["Page"]}], "PageNumber"}], CellMargins -> {{Inherited, 0}, {Inherited, Inherited

```
In[12]:= (* Integration constant is determined by requiring that  $\int_{-\infty}^{\infty} \Psi^2 dx = 1$  *)
c0[v_, x_] := Solve[Integrate[Last[Ψ[v, x]^2], {x, -∞, ∞}, Assumptions ->  $\frac{\mu v}{h} > 0$ ] == 1, C[1]]
Ψvx[v_, x_] := Ψ[v, x] /. Last[c0[v, x]]
```

```
In[14]:= (* Some of the wave functions are *)
Ψv[x_] = FullSimplify[Table[Ψ[v, x] /. Last[c0[v, x]], {v, 0, 2}]] // Flatten;
gv = Grid[Partition[Table[v, {v, 0, 2}], 1], Spacings -> {0, 2}];
gwf = Grid[Partition[Ψv[x], 1]];
gho = Grid[Partition[EnHO, 1], Spacings -> {0, 2}];
Grid[Partition[{gv, gwf, gho}, 3], Frame -> All]
```

Out[18]=

0	$\sqrt{2} e^{-\frac{2\pi^2 x^2 \mu v}{h}} \pi^{1/4} \left(\frac{\mu v}{h}\right)^{1/4}$	$\frac{h v}{2}$
1	$\frac{4 e^{-\frac{2\pi^2 x^2 \mu v}{h}} \pi^{5/4} x \sqrt{\mu} \sqrt{v} \left(\frac{\mu v}{h}\right)^{1/4}}{\sqrt{h}}$	$\frac{3 h v}{2}$
2	$-\frac{e^{-\frac{2\pi^2 x^2 \mu v}{h}} \pi^{1/4} \left(\frac{\mu v}{h}\right)^{1/4} (h - 8 \pi^2 x^2 \mu v)}{h}$	$\frac{5 h v}{2}$

```
In[19]:= (* Verify that the ground state wavefunction is indeed
the same as expressed via  $\alpha$  in the traditional treatment *)
```

$$\Psi_0[x_] = \Psi[0, x] /. Last[c0[0, x]] /. -\frac{2 \mu \pi^2 x^2 v}{h} \rightarrow \frac{-\alpha x^2}{2} /. \frac{\mu v}{h} \rightarrow \frac{\alpha}{4 \pi^2}$$

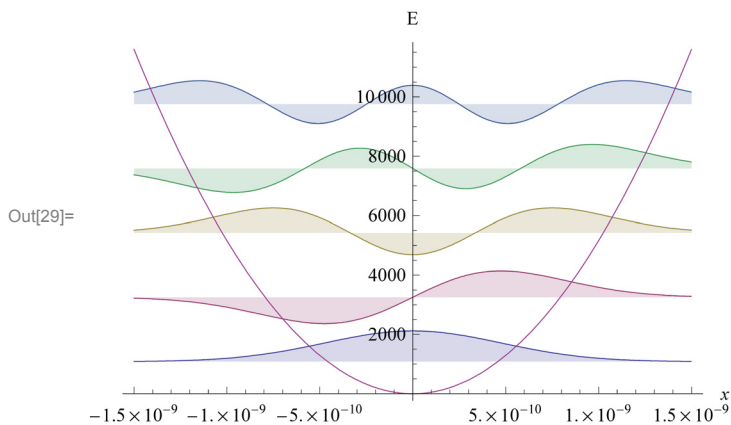
Out[19]=  $\left\{ \sqrt{2} e^{-\frac{x^2 \alpha}{2}} \pi^{1/4} \left(\frac{\mu v}{h}\right)^{1/4} \right\}$

- Next we plot the vibrational energy levels and associated wavefunctions for carbon monoxide molecule. Because of its chemical stability and permanent dipole moment, the vibrational spectrum of CO is experimentally well characterized. For consistency with the traditional infrared nomenclature, the energy on the y-axis is expressed in wavenumber ( $\text{cm}^{-1}$ ) units. The internuclear distance on the x-axis is in meters with the equilibrium internuclear distance set to zero.

```
In[20]:= << PhysicalConstants`
(* Planck Constant h in appropriate units is: *)
h = (PlanckConstant /. Joule ->  $\frac{\text{Kilogram (100 cm)}^2}{\text{Second}^2}$ ) * ( $\frac{\text{Second}}{\text{cm}^2 \text{ Kilogram}}$ );
(* Reduced mass of carbon monoxide in kilograms is: *)
μ =  $\frac{12 * 16}{12 + 16}$  ProtonMass * ( $\frac{1}{\text{Kilogram}}$ );
(* Experimental harmonic frequency in wavenumber units is: *)
waven = 2168  $\text{cm}^{-1}$  * (cm);
(* Harmonic frequency in appropriate (cm) units is: *)
ν = (waven * SpeedOfLight /. Meter -> 100 cm) * ( $\frac{\text{Second}}{\text{cm}}$ );
(* Square of the speed of light in appropriate (cm) units is: *)
cc = (SpeedOfLight2 /. Meter -> 100 cm) * ( $\frac{\text{Second}^2}{\text{cm}^2}$ );
(* Bond force constant in appropriate units is: *)
fc = k /. kharm;
```

- The first five energy levels and wave functions are shown below. Note that the magnitude of each of the wavefunctions is scaled arbitrarily to fit below the next energy level. The spacing between the energy levels is not scaled and corresponds to the experimental harmonic frequency ( $2168 \text{ cm}^{-1}$ ).

```
In[29]:= Plot[Evaluate@ Append[ Table[  $3 \cdot 10^{-2} \Psi_{\nu x}[\nu, x] + \left(\nu + \frac{1}{2}\right) \text{waven}$ , {ν, 0, 4}],  $\frac{0.006 \text{ cc fc } (x)^2}{2}$ ],
{x,  $-1.5 \cdot 10^{-9}$ ,  $1.5 \cdot 10^{-9}$ }, Filling -> Table[ν ->  $\left(\nu - \frac{1}{2}\right) \text{waven}$ , {ν, 1, 5}], AxesLabel -> {x, "E"}]
```



```
Cell[TextData[{Cell[TextData[{ValueBox["FileName"]}], "Header"], Cell[" ", "Header", CellFrame -> {{0, 0.5}, {0, 0}}, CellFrameMargins -> 4], " ", Cell[TextData[{CounterBox["Page"]}], "PageNumber"}], CellMargins -> {{Inherited, 0}, {Inherited, Inherited
```

The first five energy levels and squares of associated wave functions are shown below. Note that the magnitude of each of the squared wavefunctions is scaled arbitrarily to fit below the next energy level. Recall that the square of the wavefunction gives the probability; the plot below thus shows probability distributions in different vibrational states. For example, the most probable bond distance in the ground state CO corresponds to the equilibrium distance at the bottom of the potential well.

In[30]:=

```
Plot[
  Evaluate@ Append[ Table[1.4 10-6 Ψv,x[v, x] * Ψv,x[v, x] + (v + 1/2) waven, {v, 0, 4}], {x, -1.5 10-9, 1.5 10-9}, Filling -> Table[v -> (v - 1/2) waven, {v, 1, 5}],
  AxesLabel -> {x, "E"}, PlotRange -> All]
```

Out[30]=

