# Quantum Chemistry by Levine

LuMg

Sep 2023

## 1 Chapter 4 The Harmonic Oscillator

**4.1**
It is a Taylor series.
$f = \Sigma_0^{\inf} \frac{f^{(n)}(x=a)}{n!}(x-a)^n$

**4.2**
given the equation in 4.1
(a) $sinx = x - \frac{x^3}{3!} + \frac{x^5}{5!}$
$sinx = \Sigma_{k=0}^{\inf}(-1)^k \frac{x^{2k+1}}{(2k+1)!}$
(b) $cosx = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \dots$
$cosx = \Sigma_{k=0}^{\inf}(-1)^{2k} \frac{x^{2k}}{(2k)!}$

**4.3**
given the equation in 4.1
(a)$e^x = 1 + x + \frac{x^2}{2!} + \dots$
(b)$e^{ix} = 1 + ix - \frac{x^2}{2} + \dots = cosx + sinx$
$e^{-ix} = 1 - ix - \frac{x^2}{2} + \dots = cosx - sinx$
summing up:
$cosx = 1 - \frac{x^2}{2} + \dots$

**4.4**
$E = T + V$
$V = 2\pi^2\nu^2 mx^2$
$T = \frac{1}{2}m(\frac{dx}{dt})^2$
$x = Asin(2\pi\nu t + b)$
Combining equations above:
$E = \frac{1}{2}kA^2 = 2\pi^2\nu^2 mA^2$

**4.5**

(a) The original equation is:
$(1-x^2)y'' - 2xy' + 3y = 0$
Suppose:
$y = \Sigma_{k=0}^{\inf} c_n x^n$
$c_{n+2} = \frac{n^2+n-3}{(n+1)(n+2)} c_n$
(b) $c_4 = \frac{3}{12} \frac{-3}{2} c_0 = \frac{-3}{8} c_0$
$c_5 = \frac{9}{20} \frac{-1}{6} c_1 = \frac{-3}{40} c_1$

**4.6**

(a) odd
(b) even
(c) odd
(d) neither
(e) even
(f) odd
(g) neither
(h) even

**4.7**

Let $f(x), g(x)$ are odd functions, $k(x), l(x)$ are even functions.
$f(x)g(x) = -f(-x) * [-g(-x)] = f(-x)g(-x)$
$k(x)l(x) = k(-x)l(-x)$
$f(x)k(x) = -f(-x)k(-x)$

**4.8**

(a) Given $f(x) = f(-x)$
$\frac{df(x)}{dx} = \frac{df(-x)}{dx} = \frac{df(-x)}{d(-x)}$
$\frac{df(x)}{dx} = -\frac{df(-x)}{d(-x)}$
(b)Given $f(x) = -f(-x)$
$\frac{df(x)}{dx} = -\frac{df(-x)}{dx} = -\frac{f(x)}{dx} \ \frac{df(-x)}{dx} = \frac{df(x)}{dx}$
(c) Given $f(x) = f(-x)$
$\frac{df(x)}{dx} = -\frac{df(x)}{dx}$
$f'(0) = 0$

**4.9**

(a) in the lowest energy state:
$\Psi_0 = \frac{\alpha}{\pi}^{1/4} e^{-\alpha x^2/2}$
$< T >= \int_{-\inf}^{\inf} \Psi^* T \Psi d\tau$
$=$

$frac\alpha\pi^{1/2}int_{-\inf}^{\inf}e^{-\alpha x^2/2}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2})e^{-\alpha x^2/2}$
$= h\nu/4$
Given in this energy state $E = \frac{1}{2}h\nu$:
$< V >= \frac{h\nu}{4}$
Elsewise we can also use the integration for $< V >$:
$< V >= \int_{-\inf}^{\inf}\Psi^* T\Psi d\tau$
where: $T = 2\pi^2\nu^2 mx^2$
$< V >= \frac{h\nu}{4}$
So:
$< V >=< T >$

**4.10**
(a)for $v = 1$
$\Psi = c_1 xe^{-\alpha x^2/2}$
Normalize it:
$1 = \int_{-\inf}^{\inf}|\Psi|^2 dx$
$c_1 = \sqrt{2}\alpha^{3/4}\pi^{-1/4}$
(b) for $v = 2$
$\Psi = (c_0 + c_2 x^2)e^{-\alpha x^2/2}$
Given the recursive equation:
$c_2 = -2\alpha c_0$
For normalization:
$c_0 = 2^{-1/2}\frac{\alpha}{\pi}^{1/4}$

**4.11**
Given $v = 3$
$\Psi = (c_1 x + c_3 x^3)e^{-\alpha x^2/2}$
From the recursion:
$c_3 = -2\alpha c_1/3$
For normalization:
$1 = \int_{-\inf}^{\inf}|\Psi|^2 d\tau$
$|c_1| = \sqrt{3}\alpha^{3/4}\pi^{-1/4}$

**4.12**
for $v = 4$
$\Psi = e^{-\alpha x^2/2}(c_0 + c_2 x^2 + c_4 x^4)$
using recursive equation:
$c_2 = -4\alpha c_0$
$c_4 = \frac{4}{3}\alpha^2 c_0$
For normalization:
$1 = \int_{-\inf}^{\inf}|\Psi|^2 d\tau$

$\Psi_4 = c_0 e^{-\alpha x^2/2}(1 - 4\alpha x^2 + \frac{4}{3}\alpha^2 x^4)$

**4.13**
for $v = 1$
$\Psi = c_1 x e^{-\alpha x^2/2}$
the max prob point is:
$\frac{d|\Psi|^2}{dx} = 0$
where $x = 0$ is the min point
$x = \frac{1}{\sqrt{\alpha}}$ and $x = -\frac{1}{\sqrt{\alpha}}$ are the max point

**4.14**
for $v = 5$
it is an odd function, and has 6 max/min points

**4.15**
for quantum number $v$. the function:
$\Psi = e^{-\alpha x^2/2}(c_0 + c_2 x^2 + c_4 x^4 + \dots)$ for even $v$
$\Psi = e^{-\alpha x^2/2}(c_1 x + c_3 x^3 + c_5 x^5 + \dots)$ for odd $v$
$< x >= \int_{-\inf}^{\inf} \Psi^* x \Psi d\tau$

**4.16**
(a) T.
odd $v$ means odd function
(b) T.
(c) F.
it can multiply by $-1$ and the function still holds.
(d) T.
$E = (v + \frac{1}{2})h\nu$
(e) T.
there is only one $v$ for each energy level.

**4.17**
for PIB, $n = n_0$ there are $n_0$ max/min points
when $n = 0$ we have $E = 0$
for harmonic oscillator, $v = 0, 1, 2 \dots$ has $v + 1$ max/min points
when $v = 0$, we have $E = \frac{1}{2}h\nu$

**4.18**
(a)the classic equation:

$x = Asin(2\pi\nu t + b)$
so:
$t = \frac{1}{2\pi\nu}(sin^{-1}(\frac{x}{A}) - b)$
(b) $dt = f(x)dx$
at the turning points, the speed of classic object is 0
So it means the object will stay static there
the time to stay there (prob density) is inf

**4.19**

for $x < 0$ it is PIB condition
$E = \frac{n^2h^2}{8ml^2}$
for $x >= 0$ it is harmonic oscillator condition:
$E = (\frac{1}{2} + v)h\nu$
for continuity $E(0) = 0$
So the harmonic oscillator has to be a odd function with $v = 2k + 1$
So overall:
$E = (2k + 1 + \frac{1}{2})h\nu$

**4.20**

(a) the Schrodinger equation becomes:
$-\frac{\hbar^2}{2m}\nabla^2\Psi + \frac{1}{2}(k_x^2 + k_y^2 + k_z^2)\Psi = E\Psi$
if $\Psi = f(x)g(y)h(z)$
then separate the variables:
$-\frac{\hbar^2}{2m}\frac{1}{f}\frac{d^2f}{dx^2} + \frac{1}{2}k_x^2 = E$
formulate it to be:
$-\frac{\hbar^2}{2m}\frac{d^2f}{dx^2} + \frac{1}{2}k_x^2 f = Ef$
which is the same as one-dimension harmonic oscillator
$E_x = (\frac{1}{2} + v_x)h\nu_x$
overall:
$E = (\frac{1}{2} + v_x)h\nu_x + (\frac{1}{2} + v_y)h\nu_y + (\frac{1}{2} + v_z)h\nu_z$
(b) when $k_x = k_y = k_z$
it means $\nu_x = \nu_y = \nu_z = \nu$
$E = (\frac{3}{2} + v_x + v_y + v_z)h\nu$
the lowest energy is $v_x = v_y = v_z = 0$ not degenerate.
$E = \frac{3}{2}h\nu$
So the lowest degeneracy is $1, 0, 0$ or $0, 1, 0$ or $0, 0, 1$

**4.21**

(a) $n = 0, 1, 2, 3$ can approve
(b) $zH_n(z) = nH_{n-1}(z) + \frac{1}{2}H_{n+1}(z)$
(c) can approve for $v = 0$
$\Psi_0 = \frac{\alpha}{\pi}^{1/4}e^{-\alpha x^2/2}$

**4.23** (a)the function:
$\Psi = e^{-\alpha x^2/2}(c_0 + c_2x^2 + c_4x^4 + \dots)$ for even $v$
$\Psi = e^{-\alpha x^2/2}(c_1x + c_3x^3 + c_5x^5 + \dots)$ for odd $v$
(b) $c_{n+2} = \frac{\alpha+2\alpha n-2mE\hbar^{-2}}{(n+1)(n+2)}c_n$

**4.24**
(a) from classic equation:
$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$
So here:
$k = 4\pi^2\nu^2\mu$ where $\mu = \frac{m_1m_2}{m_1+m_2} = \frac{1}{N}\frac{1*35}{1+35}$
$k = 481N/m$
(b) zero point vibration energy:
$E = \frac{1}{2}h\nu = 2.87 * 10^{-20}J$
(c)$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$
So $\frac{\nu_2}{\nu_1} = \frac{\sqrt{m_1}}{\sqrt{m_2}}$
where $m_2 = \frac{1}{N}\frac{2*35}{2+35}$
$\nu_2 = \sqrt{\frac{m_1}{m_2}}\nu_1 = 6.20 * 10^{13}s^{-1}$

**4.25**
(a) the emission from $v_1$ to $v_2$:
$v_{light} = (v_2 - v_1)v_e - v_ex_e(v_2^2 - v_1^2 + v_2 - v_1)$
in this problem:
from $v_1 = 0$ to $v_2 = 1$:
$v_{light} = v_e - 2v_ex_e = 2889.98cm^{-1} * c$
from $v_1 = 0$ to $v_2 = 2$:
$v_{light} = 2v_e - 6v_ex_e = 5667.98cm^{-1} * c$
$v_e = 8.69 * 10^{13}s^{-1}$
$v_ex_e = 1.559 * 10^{12}s^{-1}$
(b) from $n = 0$ to $n = 3$
$v_{light} = 3v_e - 12v_ex_e$
$\frac{1}{\lambda} = \frac{v_{light}}{c} = 8346.00cm^{-1}$

**4.26**
(a) $\Delta E = \frac{hc}{\lambda} = 6.626 * 10^{34}Js * 3 * 10^{10}cm/s * 1359cm^{-1} = 2.7 * 10^{-20}J$
this is nondegenerate, using Boltzmann distribution equation:
$\frac{N_1}{N_0} = e^{-\Delta E/kT}$
where $k$ is the Boltzmann constant
when $T = 298K$:

$\frac{N_1}{N_0} = 0.0014$
when $T = 473K$:
$\frac{N_1}{N_0} = 0.016$
(b) similarly for ICl:
$\Delta E = \frac{hc}{\lambda} = 7.57 * 10^{-21}J$
where $\lambda = 381cm^{-1}$
then $\frac{N_1}{N_0} = 0.16$ at $T = 298K$
$\frac{N_1}{N_0} = 0.31$ at $T = 473K$

**4.27**
$E_{vib} = (\frac{1}{2} + v)h\nu - (v + \frac{1}{2})^2 hv_e x_e$
given $v2 = v1 + 1$
$\frac{\Delta E}{h} = v_e - 2v_e x_e(v_1 + 1)$