Quantum Chemistry by Levine

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1 Chapter 8 The Variation Method

8.1
should be less than the ground state energy
$E \leq -203.2eV$

8.2
(a) Given only V varies from 0 to l:
$< \Psi|H|\Psi > = < \Psi|T|\Psi > + < \Psi|V|\Psi >$
where from PIB condition for ground state:
$< \Psi|T|\Psi > = \frac{h^2}{8ml^2}$
$< \Psi|V|\Psi > = \int_{l/4}^{3l/4} \Psi^* V_0 \Psi dx = 0.818 \frac{\hbar^2}{ml^2}$
So $< \Psi|H|\Psi > = 5.75 \frac{\hbar^2}{ml^2}$

(b) similar as the method in (a)
$< \Psi|T|\Psi > = \int_0^l x(l-x) \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}(x(l-x))dx = 0.16667 \frac{\hbar^2 l^3}{m}$
$< \Psi|V|\Psi > = \int_{l/4}^{3l/4} V_0 x^2 (l-x)^2 dx = 0.0264 \frac{\hbar^2 l^3}{m}$
So $< \Psi|H|\Psi > = 0.193 \frac{\hbar^2 l^3}{m}$
And $\int_0^l x^2(l-x)^2 dx = \frac{l^5}{30}$
then $W = 5.79 \frac{\hbar^2}{ml^2}$

8.3
the idea is:
$< \Psi|H|\Psi > = < \Psi|T|\Psi > + < \Psi|V|\Psi >$
$= \int_0^\infty \Psi^* (\frac{-\hbar^2}{2m} \frac{d^2}{dx^2}) \Psi dx + \int_0^\infty \Psi^* (2\pi^2 \nu^2 m \Psi^2 dx)$

8.4
this is not a well-behaved function

8.5

$\Psi = x(a-x)y(b-y)z(c-z)$

$\int \Psi^* \Psi d\tau = \frac{a^5}{30}\frac{b^5}{30}\frac{c^5}{30}$

$\int \Psi^* \hat{H} \Psi d\tau$

According to variation method:

$\frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{5h^2}{4\pi m}(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2})$

the true function is $\frac{h^2}{8m}(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2})$

the error is 1.3%

8.6

Given $\Psi = b - r$

$\int \Psi^* \Psi dtau = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} (b-r)^2 r^2 sin\theta dr d\theta d\phi = \frac{2\pi b^5}{15}$

$\int \Psi \hat{H} \Psi d\tau = \int_0^{2\pi} \int_0^{\pi} \int_0^{b} (b-r)(-\frac{\hbar^2}{2m}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr})(b-r)) dr d\theta d\phi = \frac{h^2 b^3}{6\pi m}$

So:

$\frac{\int \Psi \hat{H} \Psi d\tau}{\int \Psi^* \Psi dtau} = 0.1266 \frac{h^2}{mb^2}$

Compared to the true function:

$E_1 = 0.125 \frac{h^2}{mb^2}$

8.7

there is nothing to do with other info

$\frac{\partial W}{\partial c} = 0$

8.8

(a) $V = -\infty$ at $x < 0$, so $V = 0$ when $x = 0$

(b) Given $\Psi = xe^{-cx}$

$< \Psi | \Psi >= \int_0^{\infty} x^2 e^{-2cx} dx$

$< \Psi | V | \Psi >= \int_0^{\infty} bx x^2 e^{-2cx} dx$

$< \Psi | T | \Psi >= \int_0^{\infty} xe^{-cx} (\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}) xe^{-cx} dx$

So: $W = \frac{3b}{2c} + \frac{\hbar^2 c^2}{2m}$

find the minimum of this function at $\frac{\partial W}{\partial c} = 0$

$c = \frac{3bm}{2\hbar^2}^{1/3}$

So $W = 1.96 \frac{b^2 \hbar}{m}^{1/3}$

8.9

using normalization:

$\Psi_1 = N_1 a(f + \frac{b}{a} g)$

$\Psi_2 = f + cg$

8.10

Given the variation function:$\Psi = e^{-cr}$

$\int \Psi^* \Psi d\tau = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} e^{-2cr} r^2 sin\theta dr d\theta d\phi = \frac{\pi}{c^3}$

$\int \Psi^* \hat{H} \Psi d\tau = \int e^{-cr} (\frac{-\hbar^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 r}) e^{-cr} d\tau$

$W = \frac{\hbar^2 c^2}{2\mu} - \frac{Ze^2 c}{4\pi\epsilon_0}$

using $\frac{\partial W}{\partial c} = 0$

$c = \frac{Ze^2\mu}{4\pi\epsilon_0\hbar^2}$

$W = \frac{Z^2 e^4 \mu}{2(4\pi\epsilon_0\hbar)^2}$

there is no error

8.11

Guess $\Psi = e^{-bx^2}$

$\int \Psi^* \Psi d\tau = \sqrt{\frac{\pi}{2b}}$

where $H = T + V = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + cx^4$

$\int \Psi^* \hat{H} \Psi d\tau$

$W = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{\hbar^2 b}{2m} + \frac{3c}{16b^2}$

to find the minimum of W:

$\frac{\partial W}{\partial c} = 0$

$W = 0.681 \hbar \frac{c\hbar}{m^2}^{1/3}$

8.12

Given $\Psi = x^k (l - x)^k$

$\int \Psi^* \Psi d\tau = i^{4k+1} \frac{\tau^2_{2k+1}}{\tau_{4k+2}}$

Since $V = 0$, $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$

$\int \Psi^* \hat{H} \Psi d\tau$

$W = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{h^2(4k^2+k)}{4\pi^2 m l^2 (2k-1)}$

To find optimal k:

$\frac{\partial W}{\partial k} = 0$

$k = 1.11$

$W = 0.1253 \frac{h^2}{ml^2}$

8.13

Given the wave function $\Psi = sin(x \frac{x+c}{l+2c})$

We have $\int_{-c}^{l+c} \Psi^2 dx = \frac{l+2c}{2}$

$< \Psi | V | \Psi > = \int_{-c}^{0} V_0 \Psi^2 dx + \int_{l}^{l+c} V_0 \Psi^2 dx$

$< \Psi | T | \Psi > = \int_{-c}^{l+c} \Psi (\frac{-\hbar^2}{2m} \frac{d^2}{dx^2}) \Psi dx$

So $W = \frac{<\Psi|T|\Psi> + <\Psi|T|\Psi>}{<\Psi|\Psi>} = \frac{h^2}{8m(l+2c)^2} + \frac{2V_0 c}{l+2c} - \frac{V_0}{\pi} sin(\frac{\pi l}{l+2c})$

To minimize W using $\frac{\partial W}{\partial c} = 0$

8.14

the equation only holds when $E = E_1$

8.16

Given the triangular function:
$< \Psi|\Psi >= \int_0^{l/2} x^2 dx + \int_{l/2}^{l} (l-x)^2 dx$
$< \Psi|H|\Psi >= 0.152\frac{h^2}{ml^2}$

8.17

Given the wave function:
$\Psi = e^{-cr^2/a_0^2}$
Then:
$\int_0^{\infty} \Psi^* \Psi r^2 dr = \frac{\pi}{2c}^{3/2} a_0^3$
where $H = T + V$ in spherical coordinate:
$T = -\frac{\hbar^2}{2m}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr})$
$V = -\frac{Ze^2}{4\pi\epsilon_0 r}$
So $\int \Psi^* \hat{H} \Psi d\tau = \int \Psi(T+V)\Psi d\tau$
$W = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int_0^{\infty} \Psi^* \Psi r^2 dr}$
find the smallest c that:
$\frac{\partial W}{\partial c} = 0$
$W = 0.4244\frac{Z^2 e^2}{4\pi\epsilon_0 a_0}$
where the true wave function is $\Psi = 0.5\frac{Z^2 e^2}{4\pi\epsilon a_0}$
the error is 15.1%

8.19

(a)$\begin{vmatrix} 3 & 1 & i \\ -2 & 4 & 0 \\ 5 & 7 & 1/2 \end{vmatrix}$ =i$\begin{vmatrix} -2 & 4 \\ 5 & 7 \end{vmatrix}$+1/2$\begin{vmatrix} 3 & 1 \\ -2 & 4 \end{vmatrix}$=7-34i

(b)$\begin{vmatrix} 2 & 5 & 1 & 3 \\ 8 & 0 & 4 & -1 \\ 6 & 6 & 6 & 1 \\ 5 & -2 & -2 & 2 \end{vmatrix}$

8.20

(a) $\begin{vmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ 0 & a_{22} & \dots & a_{2n} \\ \dots & & & \\ 0 & \dots & \dots & a_{nn} \end{vmatrix} = a_{11} \begin{vmatrix} a_{22} & \dots & a_{2n} & \\ 0 & \dots & a_{33} & \dots \\ \dots & & & \\ 0 & \dots & \dots & a_{nn} \end{vmatrix} = a_{11}a_{22}a_{33}\dots a_{nn}$

8.21

Given a 3-order determinant to try:

$$\begin{vmatrix} a_{11} & a_{12} & 0 \\ a_{21} & a_{22} & 0 \\ 0 & 0 & a_{33} \end{vmatrix} = a_{11}a_{22}a_{33} - a_{12}a_{21}a_{33} = a_{33}(a_{11}a_{22} - a12a_{21})$$

8.23

convert this into a determinant:

$$\begin{vmatrix} 2 & -1 & 4 & 2 & 16 \\ 3 & 0 & -1 & 4 & -5 \\ 2 & 1 & 1 & -2 & 8 \\ -4 & 6 & 2 & 1 & 3 \end{vmatrix}$$

8.24

the accuracy of float number in computer

8.26

(a) $\begin{vmatrix} 8 & -15 \\ -3 & 4 \end{vmatrix} = 77 > 0$

So $x = 0, y = 0$

(b) $\begin{vmatrix} -4 & 3i \\ 5i & \frac{15}{4} \end{vmatrix} = 0$

$x = c, y = \frac{4}{3i}c$

8.27

(a) $\begin{vmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \\ 2 & 3 & 1 \end{vmatrix} = \begin{vmatrix} 1 & 2 & 3 \\ 0 & -5 & -7 \\ 0 & -1 & -5 \end{vmatrix} = \begin{vmatrix} 1 & 2 & 3 \\ 0 & -5 & -7 \\ 0 & 0 & -\frac{18}{5} \end{vmatrix} != 0$

So $x = 0, y = 0, z = 0$

(b) $\begin{vmatrix} 1 & 2 & 3 \\ 1 & -1 & 1 \\ 7 & -1 & 11 \end{vmatrix} = \begin{vmatrix} 1 & 2 & 3 \\ 0 & -3 & -2 \\ 0 & -15 & -10 \end{vmatrix} = \begin{vmatrix} 1 & 2 & 3 \\ 0 & -3 & -2 \\ 0 & 0 & 0 \end{vmatrix} = 0$

So it has a non-trivial solution.

8.29

(a)F
(b)T
(c)F
(d)F

8.30

using the similar equation $det(H_{ij} - S_{ij}W) = 0$

$$\begin{vmatrix} 4a - 2bW & a - bW \\ a - bW & 6a - 3bW \end{vmatrix} = 0$$

Given two roots referring to E_1 and E_2:

$W_1 = 1.71a/b$ and $W_2 = 2.69a/b$

for example E_1 gives the evaluation:

$(4a - 2bW_1)c_1 + (a - bW)c_2 = 0$

$(a - bW_1)c_1 + (6a - 3bW)c_2 = 0$

and $< c_1 f_1 | c_2 f_2 >= 1$ as normalization:

$c_1 = 0.42\frac{1}{\sqrt{b}}, c_2 = 0.34\frac{1}{\sqrt{b}}$

similarly for E_2:

$(4a - 2bW_2)c_1 + (a - bW_2)c_2 = 0$

$(a - bW_2)c_1 + (6a - 3bW_2)c_2 = 0$

$c_1 = -0.85\frac{1}{\sqrt{b}}, c_2 = 0.70\frac{1}{\sqrt{b}}$

8.31

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W \\ H_{12} - S_{12}W & H_{11} - S_{11}W \end{vmatrix} = 0$$

So $W = \frac{H_{11}+H_{12}}{S_{11}+S_{12}}$

Adding it back to the equation:

$\frac{c_1}{c_2} = 1 or - 1$

8.33

Given $f_1 = x^2(l - x)$

$f_2 = x(l - x)^2$

So $S_1 1 =< f_1|f_1 >= \frac{l^7}{105}$

$S_1 2 =< f_1|f_2 >= \frac{l^7}{140}$

$S_2 2 =< f_2|f_2 >= \frac{l^7}{105}$

$H_{11} =< f_1|H|f_1 >= \frac{l^5\hbar^2}{15m}$

$H_{12} =< f_1|H|f_2 >= \frac{l^5\hbar^2}{60m}$

$H_{22} =< f_2|H|f_2 >= \frac{l^5\hbar^2}{15m}$

So $W_1 = \frac{5h^2}{ml^2}$

$W_2 = \frac{21h^2}{ml^2}$

8.34

Given the $x' = x - \frac{l}{2}$

$f_1 = (\frac{l}{2} + x')(\frac{l}{2} - x')$

$f_2 = (\frac{l}{2} + x')^2(\frac{l}{2} - x')^2$

$f_3 = (\frac{l}{2} + x')(\frac{l}{2} - x')(-x')$

$f_4 = (\frac{l}{2} + x')^2(\frac{l}{2} - x')^2(-x')$

8.35

Given $f_1 = x(l-x)$
$f_2 = x^2(l-x)^2$
$H_{11} =< f_1|H|f_1 >= \int_0^l x(l-x)\hat{H}x(l-x)dx$
$H_{12} =< f_1|H|f_2 >= \frac{\hbar^2 l^5}{30m}$
$H_{22} =< f_2|H|f_2 >= \frac{\hbar^2 l^7}{105m}$
$S_{12} =< f_1|f_2 >= \frac{l^7}{140}$
$S_{22} =< f_2|f_2 >= \frac{l^9}{630}$

8.36

Given $\begin{vmatrix} H_{33} - S_{33}W & H_{34} - S34W \\ H_{43} - S_{43}W & H_{44} - S44W \end{vmatrix} = 0$
$W_1 = 0.5\frac{\hbar^2}{ml^2}$
$W_2 = 2.54\frac{\hbar^2}{ml^2}$

8.41

$A^* = \begin{pmatrix} 7 & 3 & 0 \\ 2+i & -2i & -i \\ 1-i & 4 & 2 \end{pmatrix}$
$A^T = \begin{pmatrix} 7 & 2-i & 1+i \\ 3 & 2i & 4 \\ 0 & i & 2 \end{pmatrix}$
$A^{\hat{=}} \begin{pmatrix} 7 & 2+i & 1-i \\ 3 & -2i & 4 \\ 0 & -i & 2 \end{pmatrix}$

8.42

(a)F
(b)CF
(c)DF

8.45

(a)$\begin{vmatrix} 0-\lambda & -1 \\ 3 & 2-\lambda \end{vmatrix} = 0$
$\lambda_1 = 1 + \sqrt{2}i, \lambda_2 = 1 - \sqrt{2}i$

$$-\lambda_1 c_1 - c_2 = 03c_1 + (2-\lambda)c_2 = 0 \tag{1}$$

Resulting in the eigenfunction:

$c_1 = \begin{pmatrix} \frac{1}{2} \\ -\frac{1}{2} - \frac{1}{2}\sqrt{2}i \end{pmatrix}$
$c_2 = \begin{pmatrix} \frac{1}{2} \\ -\frac{1}{2} + \frac{1}{2}\sqrt{2}i \end{pmatrix}$
(b)$\begin{vmatrix} 2-\lambda & 0 \\ 9 & 2-\lambda \end{vmatrix} = 0$
So $\lambda = 2$
There is no determined eigenfunction.

(c)$\begin{vmatrix} 4-\lambda & 0 \\ 0 & 4-\lambda \end{vmatrix} = 0$
$\lambda = 4$
So there is no determined eigenfunction.

8.46
$(a_{11} - \lambda)(a_{22} - \lambda)(a_{33} - \lambda) = 0$
Generating three $\lambda = a_{11}, a_{22}, a_{33}$
Generating eigenfunction:
$c_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$
$c_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$
$c_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

8.47
$\begin{vmatrix} 2-\lambda & 2 \\ 2 & -1-\lambda \end{vmatrix} = 0$
$\lambda_1 = 3, \lambda_2 = -2$
So the first eigenfunction:
$\begin{pmatrix} \frac{2}{\sqrt{5}} \\ \frac{1}{\sqrt{5}} \end{pmatrix}$
the other eigenfunction is:
$\begin{pmatrix} \frac{2}{\sqrt{5}} \\ -\frac{1}{\sqrt{5}} \end{pmatrix}$

8.66 (a)True
(b)True
(c)True
(d)True

(e)True
(f)True
(g)True
(h) False
(i)True
(j)False
(k)False
(l)True
(m)True
(n)True