PROBLEM SET SOLUTIONS

CHAPTER 8, Levine, *Quantum Chemistry,* 5th Ed.

8.27(a) For the ground state of the hydrogen atom use the

Gaussian trial function $\phi = \exp\,[-cr^2/(a_0^{\,2})]$.

Find the optimum value of c and the percent error in the energy.

(b) Multiply the trial function by the Spherical Harmonic $Y_2^{\,0}$, and the minimize the variational integral. This yields an upper bound to the energy of which hydrogen atom state?

- c is variable parameter. Find c by minimizing I with respect to c:

$\partial I/\partial c = 0$.

For the H atom, $H = -\underline{h}^2/(2\mu^2)\ \nabla^2 - Z\,(e')^2/r$,

$\nabla^2 = \partial^2/\partial r^2 + (2/r)\ \partial/\partial r - L^2/(r^2\underline{h}^2)$

$L^2 \phi = L^2 \exp[-cr^2/(a_0^2)] = 0$ since ϕ has no angular dependence.

$\mu \sim m_e \rightarrow a_0 = \underline{h}^2/[m_e(e')^2]$

Let $c' = c/a_0^2 \rightarrow \phi = \exp[-c'r^2]$

$H\phi = -\underline{h}^2/(2m_e^{\ 2}) \{-6c'r^2 \exp[-c'r^2] + 4(c')^2 r^2 \exp[-c'r^2]\}$

$- \{Z(e')^2/r\} \exp[-c'r^2]$

$\int\phi^* H\phi \, d\tau = -(\underline{h}^2/m_e)(3/16)(\pi/c'')^{1/2} - (e')^2/[2c''], \; c'' = 2c'$

$\int\phi^*\phi \, d\tau = \pi^{1/2}/[4c''^{3/2}]$

$I = \int\phi^* H\phi \, d\tau / \int\phi^*\phi \, d\tau = \underline{h}^2 3c''/(4m_e) - 2(e')^2(c''/\pi)^{1/2}$

$\partial I/\partial c = (\partial I/\partial c'')(\partial c''/\partial c) = (\partial I/\partial c'')(2/a_0^2) = 0$ if $(\partial I/\partial c'') = 0$

$(\partial I/\partial c'') = \underline{h}^2 3/(4m_e) - 2(e')^2(1/2)/(c''\pi)^{-1/2} \rightarrow$

$c'' = (e')^4 m_e^2 16/[\pi \underline{h}^4 9] = 2c/a_0^2 \rightarrow c = a_0^2 (e')^4 m_e^2 16/[2\pi \underline{h}^4 9]$

$a_0 = \underline{h}^2/[m_e(e')^2] \rightarrow c = 8/(9\pi)$

$I = \int\phi^* H\phi \, d\tau / \int\phi^*\phi \, d\tau \geq E_1$ (n = 1 ground state of H atom)

Use the value for c to evaluate I:

$I = - a_0^2(e')^2(9\pi/64) /\{ a_0^3(27\pi^2/256)\} = -0.424\ (e')^2/a_0$

For H atom, $E_n = -Z^2 m_e(e')^4/[2n^2\ \underline{h}^2]$

$E_1 = - m_e(e')^4/[2\underline{h}^2]$

% error = $|I - E_1| / |E_1| \times 100 = |0.424 - 0.500|/(0.500)\times100$

$= 15\%$

8.14 (b) $\phi = \exp[-cr^2/ (a_0^2)]\ Y_2^0$

$L^2\phi = \exp[-cr^2/ (a_0^2)]\ L^2\ Y_2^0$

$= \exp[-cr^2/ (a_0^2)]\ [2\ (2+1)\ \underline{h}^2]Y_2^0$

$= 6\ \underline{h}^2\phi$

$H = -\underline{h}^2/(2\mu^2)\ \nabla^2 - Z\ (e')^2/r,$

$\nabla^2 = \partial^2/\partial r^2 + (2/r)\ \partial/\partial r - L^2/(r^2\underline{h}^2)$

$H\ \phi = -\underline{h}^2/(2m_e)\ \{-6c'r^2 \exp[-c'r^2]\ Y_2^0 + 4(c')^2r^2 \exp[-c'r^2]\ Y_2^0$

$- (6/r^2) \exp[-c'r^2]\ Y_2^0\} - \{Z\ (e')^2/r\} \exp[-c'r^2]\ Y_2^0$

$\int\phi^*H\phi\ d\tau = (\underline{h}^2/m_e)\ (3/16)\ (\pi/c'')^{1/2} - (e')^2/[2\ c'']$ (from Part a)

$+ 6\underline{h}^2/(2m_e) \int_0^\infty \exp[-c'r^2]\ dr,\ \ (c'' = 2c' = 2c/ a_0^2)$

$= (\underline{h}^2/m_e) (27/16) (\pi/c'')^{1/2} - (e')^2/[2 c'']$

Note: $\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, Y_2^{0*} Y_2^0 = 1$

$\int\phi^*\phi \, d\tau = \pi^{1/2}/[4c''^{3/2}]$ (from Part a because Spherical Harmonics

are normalized

$I = \int\phi^* H\phi \, d\tau / \int\phi^*\phi \, d\tau = \{(\underline{h}^2/m_e) (27/16) (\pi/c'')^{1/2}$

$- (e')^2/[2 c'']\}/\{\pi^{1/2}/[4c''^{3/2}]\} = \underline{h}^2 27c''/(4 m_e) - 2(e')^2(c''/\pi)^{1/2}$

$\partial I/\partial c = (\partial I/\partial c'') (\partial c''/\partial c) = (\partial I/\partial c'') (2/a_0^2) = 0$ if $(\partial I/\partial c'') = 0$

$(\partial I/\partial c'') = \underline{h}^2 27/(4m_e) - 2(e')^2(1/2)/(c''\pi)^{-1/2} \rightarrow$

$c'' = (e')^4 m_e^2 16/[\pi \underline{h}^4 27^2] = 2c/a_0^2 \rightarrow$

$c = (a_0^2/2)(e')^4 m_e^2 16/[\pi \underline{h}^4 27^2]$

$a_0 = \underline{h}^2/[m_e(e')^2] \rightarrow c = 8/(27^2\pi)$

$I = \int\phi^* H\phi \, d\tau / \int\phi^*\phi \, d\tau \geq E_?$ $\quad$ $n = ?$

For $c = 8/(27^2\pi)$, $\int\phi^* H\phi \, d\tau = (27^2/64)\pi a_0^2(e')^2$

For $c = 8/(27^2\pi)$, $\int\phi^*\phi \, d\tau = - \pi^2 a_0^3 27^3/256$

$I = \int\phi^* H\phi \, d\tau / \int\phi^*\phi \, d\tau = - (0.148/\pi) (e')^2/ a_0$

$E_n = -Z^2 m_e(e')^4/[2n^2 \underline{h}^2] = -[0.500 (e')^2/ a_0]/n^2$, $Z = 1$

$0.500/ n^2 \sim 0.148/\pi$ if $n = 3$. So have upper bound to $n = 3$ state.

8.28 Apply the linear variation function

$$\phi = c_1x^2(L - x) + c_2x(L-x)^2 \qquad 0 \leq x \leq L$$

to the particle in a one-dimensional box. Calculate the percent error for the n = 1 and n = 2 energies. Sketch $x^2(L - x)$, $x(L-x)^2$, and the two apprxiate functions that you obtain. (To help sketch the functions find the nodes and the maxima and minima.)

Let $\phi = c_1f_1 + c_2f_2$ where $f_1 = x^2(L - x)$, $f_2 = x\,(L - x)^2$

Solve for the two lowest energies by setting

$$\sum_{k=1,2} c_k\,(H_{ik} - S_{ik}\,I) = 0,\ i = 1,2;\ I = \text{variational energy},$$

$H_{ik} = \langle f_i | H | f_k \rangle$, $S_{ik} = \langle f_i | f_k \rangle$.

This has a nontrivial solution if the determinant of the coeffcients of the c's equals 0:

$$\begin{vmatrix} (H_{11} - S_{11}\,I) & (H_{12} - S_{12}\,I) \\ (H_{21} - S_{21}\,I) & (H_{22} - S_{22}\,I) \end{vmatrix} = 0$$

or $(H_{11} - S_{11}\,I)\,(H_{22} - S_{22}\,I) - (H_{12} - S_{12}\,I)\,(H_{21} - S_{21}\,I) = 0$

which gives a quadratic equation for I:

$A I^2 + B I + C = 0$,

$I = -B/(2A) \pm \{SQRT (B^2 - 4AC)\}/(2A)$ with

$A = S_{11} S_{22} - S_{21} S_{12}$

$B = S_{21} H_{12} + S_{12} H_{21} - (S_{11} H_{22} + S_{22} H_{11})$

$C = H_{11} H_{22} - H_{12} H_{21}$

Evaluate the integrals & solve for I_1 & I_2:

$S_{ik} = \langle f_i | f$

$A = S_{11}\, S_{22} - S_{21}\, S_{12}$

$= S_{11}^2 - S_{21}^2 = L^{14}\, (3.\ 96 \times 10^{-5})$

$B = S_{21}\, H_{12} + S_{12}\, H_{21} - (S_{11}\, H_{22} + S_{22}\, H_{11})$

$= 2\, (S_{21}\, H_{12} - S_{11}\, H_{22})$

$= -\, \{\underline{h}^2/(2m)\}\; 2\, L^{1/2}\, (10.32 \times 10^{-4})$

$C = H_{11}\, H_{22} - H_{12}\, H_{21}$

$= H_{11}^2 - H_{12}^2 = -\, \{\underline{h}^2/(2m)\}\; L^{10}\, (0.0167)$

$I = \{(2.06 \pm 1.26)/7.92\}\; 10^2\; \{\underline{h}^2/(2m\, L^2)\}$

$I_1 = 0.101\text{x}10^2\; \{\underline{h}^2/(2m\, L^2)\} \geq E_1$

$I_2 = 0.419\text{x}10^2\; \{\underline{h}^2/(2m\, L^2)\} \geq E_2$

Calculate % error in energy:

For a particle in a one-dimensional box:

$E_n = n^2\, h^2/(8m\, L^2)$, $\qquad \underline{h} = h/(2\pi)$

$I_1 = 10.1\; \{\underline{h}^2/(2m\, L^2)\} = 10.1\; h^2/(4\pi^2\, 2m\, L^2)$

$= (10.1/\pi^2)\; h^2/(8m\, L^2) = 1.02\; h^2/(8m\, L^2)$

$E_1 = h^2/(8m\ L^2)$

% error = $(|I_1 - E_1| / E_1) \times 100 = (1.02 - 1) \times 100 = 2\%$

$I_2 = 41.9\ \{\underline{h}^2/(2m\ L^2)\} = 41.9\ h^2/(4\pi^2 2m\ L^2)$

$= (41.9/\pi^2)\ h^2/(8m\ L^2) = 4.25\ h^2/(8m\ L^2)$

$E_2 = 4\ h^2/(8m\ L^2)$

% error = $(|I_2 - E_2| / E_2) \times 100 = [(4.25 - 4)/4] \times 100 = 6.25\%$

Find ϕ_1 by finding the c_1 & c_2 that correspond to I_1. Repeat for ϕ_2 and I_2. Note: c_1 & c_2 for ϕ_1 are DIFFERENT from c_1 & c_2 for ϕ_2

$$\sum_{k=1,2} c_k\ (H_{ik} - S_{ik}\ I_1) = 0,\ i = 1,2$$

Discard one of the two eq. For example, use the eq. with I = 1:

$c_1\ (H_{11} - S_{11}\ I_1) + c_2\ (H_{12} - S_{12}\ I_1) = 0$

Solve for c_2 in terms of c_1:

$$c_2 = -\ c_1\ (H_{11} - S_{11}\ I_1)/\ (H_{12} - S_{12}\ I_1)$$

Then solve for c_1 by normalizing ϕ_1:

$$< \phi_1 | \phi_1 > = 1 = \int_0^L (c_1 f_1 + c_2 f_2)^2\ dx$$

$1 = \ c_1^2 \{S_{11} + S_{22} [H_{11} - S_{11} I_1)/(H_{12} - S_{12} I_1)]^2$

$- 2 S_{12} (H_{11} - S_{11} I_1)/(H_{12} - S_{12} I_1)\}$

$= c_1^2 \{L^7/105 + (L^7/105) (-0.949)^2 - 2(L^7/140) (-0.949)\}$

$= c_1^2 L^7 (0.0317)$

$c_1 = 5.62/ L^{7/2}$

$c_2 = - c_1 (H_{11} - S_{11} I_1)/ (H_{12} - S_{12} I_1) = - c_1 (-0.949) = 5.33/ L^{7/2}$

$\phi_1 = c_1 f_1 + c_2 f_2 = (5.62/ L^{7/2}) f_1 + c_2 (5.33/ L^{7/2})$

is an approximation to the ground state wavefunction for the particle in a one-dimensional box

Find ϕ_2 the same way, but use I_2:

Discard one of the two eq. For example, use the eq. with I = 2:

$c_1 (H_{11} - S_{11} I_2) + c_2 (H_{12} - S_{12} I_2) = 0$

Solve for c_2 in terms of c_1:

$c_2 = - c_1 (H_{11} - S_{11} I_2)/ (H_{12} - S_{12} I_2)$

Then solve for c_1 by normalizing ϕ_2: $\phi_2 = c_1 f_1 + c_2 f_2$

$< \phi_2 | \phi_2 > = 1 = \int_0^L (c_1 f_1 + c_2 f_2)^2 dx$

$1 = \ c_1^2 \{S_{11} + S_{22} [H_{11} - S_{11} I_2)/(H_{12} - S_{12} I_2)]^2$

$- \ 2 S_{12} (H_{11} - S_{11} I_2)/(H_{12} - S_{12} I_2)\}$

Note: The form is the same as in the ϕ_1 case but c_1 & c_2 will be different because I_2 is used instead of I_1.

$1 = c_1^2 L^7 (0.0048)$

$c_1 = 14.4/ L^{7/2}$

$c_2 = - c_1 (H_{11} - S_{11} I_2)/ (H_{12} - S_{12} I_2) = - c_1 (1) = - 14.4/ L^{7/2}$

$\phi_2 = c_1f_1 + c_2f_2 = (14.4/ L^{7/2}) f_1 + = (- 14.4/ L^{7/2}) f_2$

is an approximation to the first excited state wavefunction for the particle in a one-dimensional box

Plot the functions f_1, f_2, ϕ_1, and ϕ_2 for an arbitrary choice of L (say L=1). To do this, evaluate the functions at x = 0, L/4, L/2, 3L/4, and L:

x	0	L/4	L/2	3L/4	L
f_1	0	$3L^3/64 = 0.0469L^3$	$L^3/8 = 0.125 L^3$	$9L^3/64 = 0.140L^3$	0
f_2	0	$9L^3/64 = 0.140L^3$	$L^3/8 = 0.125 L^3$	$3L^3/64 = 0.0469L^3$	0
ϕ_1	0	$1.01/L^{1/2}$	$1.37/L^{1/2}$	$1.04/ L^{1/2}$	0
ϕ_2	0	-1.35/	0	$1.35/ L^{1/2}$	0

		$L^{1/2}$			

8.1 (3^{rd} Ed.) Use the trial function

$$\phi = \exp[-b\alpha x^2]$$

for the ground state of the harmonic oscillator. Show that minimization of the variation integral gives b = 1/2 and $E_0 \leq h\nu/2$.

Find b by minimization of I with respect to b:

$$\partial I/\partial b = 0 = \partial/\partial b\, [\int\phi^*H\phi\, d\tau/ \int\phi^*H\phi\, d\tau]$$

$$\int\phi^*\phi\, d\tau = [\pi/(2b\alpha)]^{1/2}$$

$$\partial/\partial b\, [\int\phi^*\phi\, d\tau] = -\{1/(2\, b^{3/2})\}\, [\pi/(2\alpha)^{1/2}]$$

$$H = \{\underline{h}^2/(2m)\}\, (-d^2/dx^2 + \alpha^2x^2)$$

$$H\phi = \{\underline{h}^2/(2m)\}\, [2b\alpha + \alpha^2x^2\,(1 - 4b^2)]\, \exp[-b\alpha x^2]$$

$$\int\phi^*H\phi\, d\tau = \{\underline{h}^2/(2m)\}\, [b^{1/2}\,(\alpha\pi/2)^{1/2} + (1/b^{3/2})\,(\alpha\pi/2^5)^{1/2}]$$

$$\partial/\partial b\, [\int\phi^*H\phi\, d\tau] = \{\underline{h}^2/(2m)\}\, (\alpha\pi/(2b))^{1/2}\{1 - 3/(4b^2)\}$$

$$\partial I/\partial b = 0 = \{1/\int\phi^*\phi\, d\tau\}\, \partial/\partial b\, \{\int\phi^*H\phi\, d\tau\}$$

$$+ \{\int\phi^*H\phi\, d\tau\}\, \partial/\partial b\, \{1/\int\phi^*\phi\, d\tau\}$$

$b^2 = 1/4$, $b = 1/2$; $I = [\int\phi^*H\phi\, d\tau/ \int\phi^*H\phi\, d\tau] = h\nu/2$