SQ11

For $l=0$, the radial part of the Schrödinger equation is:

$$\hat{H}_r R(r) = \left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{e^2}{4\pi\epsilon_0 r}\right] R(r) = E R(r) \quad \ldots \quad (1)$$

Applying variation method with trial function:

$$\phi(r) = A e^{-\lambda r^2} \quad \ldots \quad (2)$$

where $A^2 = 8\sqrt{\frac{2\lambda^3}{\pi}}$ is a normalisation constant.

and λ is a parameter to be determined.

By variation method, we would like to find the best λ_{best} s.t. $\langle \hat{H}_r \rangle_\phi$ attains its minimum.

Compute $\langle \hat{H}_r \rangle_\phi$ in terms of λ:

$$\langle \hat{H}_r \rangle_\phi = \int_0^\infty \phi^*(r)\, \hat{H}_r\, \phi(r)\, r^2\, dr$$

$$= \int_0^\infty A^2 e^{-\lambda r^2}\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{e^2}{4\pi\epsilon_0 r}\right] e^{-\lambda r^2}\, r^2\, dr$$

$$= A^2 \int_0^\infty e^{-\lambda r^2}\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2(-2\lambda r e^{-\lambda r^2})\right) - \frac{e^2}{4\pi\epsilon_0 r} e^{-\lambda r^2}\right] r^2\, dr$$

$$= A^2 \int_0^\infty e^{-\lambda r^2}\left[-\frac{\hbar^2}{2\mu}(-2\lambda)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^3 e^{-\lambda r^2}\right) - \frac{e^2}{4\pi\epsilon_0 r} e^{-\lambda r^2}\right] r^2\, dr$$

$$= A^2 \int_0^\infty e^{-\lambda r^2}\left[\frac{\hbar^2\lambda}{\mu}\frac{1}{r^2}\left(3r^2 e^{-\lambda r^2} - 2\lambda r^4 e^{-\lambda r^2}\right) - \frac{e^2}{4\pi\epsilon_0 r} e^{-\lambda r^2}\right] r^2\, dr$$

$$= A^2 \int_0^\infty -\frac{e^2}{4\pi\epsilon_0} r e^{-2\lambda r^2} + \frac{3\hbar^2\lambda}{\mu} r^2 e^{-2\lambda r^2} - \frac{2\hbar^2\lambda^2}{\mu} r^4 e^{-2\lambda r^2}\, dr$$

With some useful Gaussian integral formula:

$$\int_0^\infty r^4 e^{-\lambda r^2} dr = \frac{3}{8\lambda^2}\sqrt{\frac{\pi}{\lambda}}, \quad \int_0^\infty r^2 e^{-\lambda r^2} dr = \frac{1}{4\lambda}\sqrt{\frac{\pi}{\lambda}}, \quad \int_0^\infty r e^{-\lambda r^2} dr = \frac{1}{2\lambda}$$

(You can check them out from table or simply do it as an exercise)

$$\therefore \langle \hat{H}_r \rangle_\phi = A^2 \left(-\frac{e^2}{4\pi\epsilon_0} \frac{1}{2(2\lambda)} + \frac{3\hbar^2 \lambda}{\mu} \frac{1}{4(2\lambda)} \sqrt{\frac{\pi}{2\lambda}} - \frac{2\lambda^2\hbar^2}{\mu} \frac{3}{8(2\lambda)^2} \sqrt{\frac{\pi}{2\lambda}} \right)$$

$$= \frac{3\lambda\hbar^2}{2\mu} - \frac{2e^2}{4\pi\epsilon_0}\sqrt{\frac{2\lambda}{\pi}} \quad \cdots (3) \quad \left(\text{Remember } A^2 = 8\sqrt{\frac{2\lambda^3}{\pi}}\right)$$

Now, we optained $\langle \hat{H}_r \rangle_\phi$ as a function of λ. (The function is sketched below)

The next step is to find the minimum $\langle \hat{H}_r \rangle_\phi$ with respect to λ:

Diff. (3) with respect to λ, and set:

$$\left.\frac{\partial \langle \hat{H}_r \rangle_\phi}{\partial \lambda}\right|_{\lambda=\lambda_{best}} = 0$$

$$\therefore \frac{3\hbar^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0}\sqrt{\frac{2}{\pi\lambda_{best}}} = 0$$

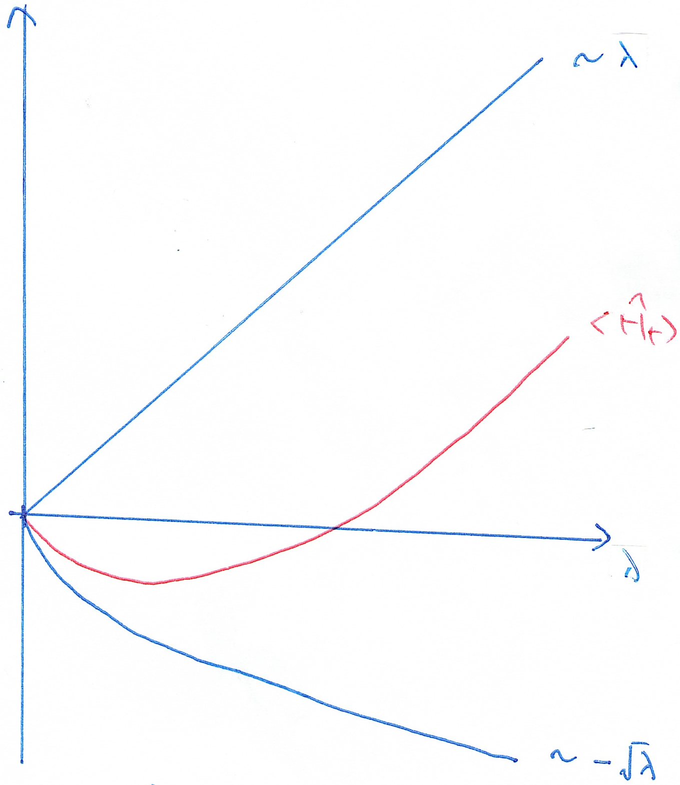
$$\sqrt{\lambda_{best}} = \frac{e^2}{4\pi\epsilon_0} \frac{2\mu}{3\hbar^2}\sqrt{\frac{2}{\pi}}$$

$$\text{or} \quad \lambda_{best} = \frac{e^4}{18\pi^3\epsilon_0^2} \frac{\mu^2}{\hbar^4}$$

The corresponding min $\langle \hat{H}_r \rangle_\phi$ is:

$$\min \langle \hat{H}_r \rangle_\phi = -\frac{4}{3\pi} \frac{\mu e^4}{\hbar^2 (4\pi\epsilon_0)^2}$$

$$\approx -0.424 \frac{\mu e^4}{\hbar^2 (4\pi\epsilon_0)^2}$$



Compared to the true value $E_{GS} = -0.5 \frac{\mu e^4}{\hbar^2 (4\pi\epsilon_0)^2}$,

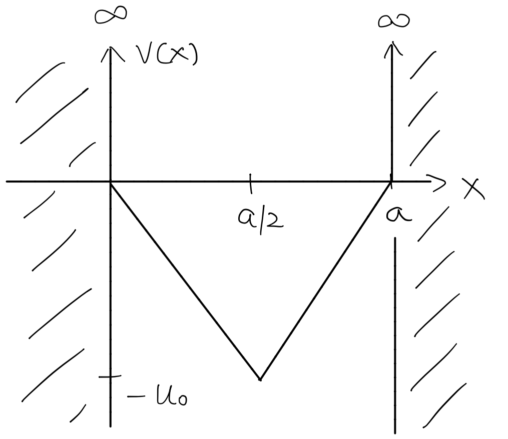
1. The result is quite close, the variational method is a good estimate to the true hydrogen system.

2. The estimated value $\min \langle \hat{H}_r \rangle_\phi$ is slightly larger than E_{GS}, since the true ground state energy should have the lowest energy level.

SQ12

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$$V(x) = \begin{cases} -\frac{2U_0}{a}x & \text{for } 0<x<\frac{a}{2} \\ \frac{2U_0}{a}x - 2U_0 & \text{for } \frac{a}{2}<x<a \\ \infty & \text{otherwise} \end{cases}$$



$$\phi_{trial}(x) = c_1\psi_1(x) + c_3\psi_3(x)$$

$$= \begin{cases} c_1\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right) + c_3\sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right) & \text{for } 0<x<a \\ 0 & \text{Otherwise} \end{cases}$$

Variational method: find the best c_1 and c_3 values which give the best estimate of E_{GS} (i.e. minimize $\langle\hat{H}\rangle_\phi = \langle\phi|\hat{H}|\phi\rangle / \langle\phi|\phi\rangle$)

Using the same notation as lecture notes:

$$E(c_1, c_3) \equiv \langle\hat{H}\rangle_\phi$$

$$H_{ij} = \int \psi_i^* \hat{H} \psi_j \, dx \qquad H_{ji}^* = H_{ij} \quad (\hat{H} \text{ is Hermitian})$$

$$S_{ij} = \int \psi_i^* \psi_j \, dx = \delta_{ij}$$

(ψ_i are normalized eigenfunctions of 1D infinite well so they are orthonormal)

By Eq (B7) in notes AM-B18,

$$\begin{pmatrix} H_{11} - ES_{11} & H_{13} - ES_{13} \\ H_{31} - ES_{31} & H_{33} - ES_{33} \end{pmatrix} \begin{pmatrix} c_1 \\ c_3 \end{pmatrix} = 0 \qquad (*)$$

SQ12

$$H_{11} = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sin\left(\frac{\pi x}{a}\right)dx + \frac{2}{a}\int_0^{a/2}\sin\left(\frac{\pi x}{a}\right)\left(\frac{-2U_0}{a}x\right)\sin\left(\frac{\pi x}{a}\right)dx$$

$$+ \frac{2}{a}\int_{a/2}^{a}\sin\left(\frac{\pi x}{a}\right)\left(\frac{2U_0}{a}x - 2U_0\right)\sin\left(\frac{\pi x}{a}\right)dx$$

$$= \frac{\hbar^2}{2m}\frac{2}{a}\frac{\pi^2}{a^2}\int_0^a \sin^2\left(\frac{\pi x}{a}\right)dx - \frac{4U_0}{a^2}\int_0^{a/2}\sin^2\left(\frac{\pi x}{a}\right)x\,dx$$

$$+ \frac{4U_0}{a^2}\int_{a/2}^{a}\sin^2\left(\frac{\pi x}{a}\right)x\,dx - \frac{4U_0}{a}\int_{a/2}^{a}\sin^2\left(\frac{\pi x}{a}\right)dx$$

$$= \frac{\hbar^2}{2m}\frac{\pi^2}{a^2} - \frac{4U_0}{a^2}\frac{a^2(\pi^2+4)}{16\pi^2} + \frac{4U_0}{a^2}\frac{a^2(3\pi^2-4)}{16\pi^2} - \frac{4U_0}{a}\frac{a}{4}$$

$$= \frac{\hbar^2}{2m}\frac{\pi^2}{a^2} - \frac{U_0(\pi^2+4)}{2\pi^2}$$

$$H_{33} = \frac{2}{a}\int_0^a \sin\left(\frac{3\pi x}{a}\right)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sin\left(\frac{3\pi x}{a}\right)dx + \frac{2}{a}\int_0^{a/2}\sin\left(\frac{3\pi x}{a}\right)\left(\frac{-2U_0}{a}x\right)\sin\left(\frac{3\pi x}{a}\right)dx$$

$$+ \frac{2}{a}\int_{a/2}^{a}\sin\left(\frac{3\pi x}{a}\right)\left(\frac{2U_0}{a}x - 2U_0\right)\sin\left(\frac{3\pi x}{a}\right)dx$$

$$= \frac{\hbar^2}{2m}\frac{2}{a}\frac{9\pi^2}{a^2}\int_0^a \sin^2\left(\frac{3\pi x}{a}\right)dx - \frac{4U_0}{a^2}\int_0^{a/2}\sin^2\left(\frac{3\pi x}{a}\right)x\,dx$$

$$+ \frac{4U_0}{a^2}\int_{a/2}^{a}\sin^2\left(\frac{3\pi x}{a}\right)x\,dx - \frac{4U_0}{a}\int_{a/2}^{a}\sin^2\left(\frac{3\pi x}{a}\right)dx$$

$$= \frac{\hbar^2}{2m}\frac{9\pi^2}{a^2} - \frac{4U_0}{a^2}\frac{a^2(9\pi^2+4)}{144\pi^2} + \frac{4U_0}{a^2}\frac{a^2(27\pi^2-4)}{144\pi^2} - \frac{4U_0}{a}\frac{a}{4}$$

$$= \frac{\hbar^2}{2m}\frac{9\pi^2}{a^2} - \frac{U_0(9\pi^2+4)}{18\pi^2}$$

SQ12

$$H_{13} = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sin\left(\frac{3\pi x}{a}\right)dx + \frac{2}{a}\int_0^{a/2}\sin\left(\frac{\pi x}{a}\right)\left(-\frac{2u_0}{a}x\right)\sin\left(\frac{3\pi x}{a}\right)dx$$

$$+ \frac{2}{a}\int_{a/2}^{a}\sin\left(\frac{\pi x}{a}\right)\left(\frac{2u_0}{a}x - 2u_0\right)\sin\left(\frac{3\pi x}{a}\right)dx$$

$$= \frac{\hbar^2}{2m}\frac{2}{a}\frac{9\pi^2}{a^2}\int_0^a \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{3\pi x}{a}\right)dx - \frac{4u_0}{a^2}\int_0^{a/2}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{3\pi x}{a}\right)x\,dx$$

$$+ \frac{4u_0}{a^2}\int_{a/2}^{a}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{3\pi x}{a}\right)x\,dx - \frac{4u_0}{a}\int_{a/2}^{a}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{3\pi x}{a}\right)dx$$

$$= -\frac{4u_0}{a^2}\left(-\frac{a^2}{4\pi^2}\right) + \frac{4u_0}{a^2}\left(\frac{a^2}{4\pi^2}\right)$$

$$= \frac{2u_0}{\pi^2}$$

$$H_{31} = H_{13}^* = \frac{2u_0}{\pi^2}$$

$\therefore$ (*) becomes

$$\begin{pmatrix} H_{11} - ES_{11} & H_{13} - ES_{13} \\ H_{31} - ES_{31} & H_{33} - ES_{33} \end{pmatrix}\begin{pmatrix} c_1 \\ c_3 \end{pmatrix} = 0$$

$$\begin{pmatrix} \frac{\hbar^2}{2m}\frac{\pi^2}{a^2} - \frac{u_0(\pi^2+4)}{2\pi^2} - E & \frac{2u_0}{\pi^2} \\ \frac{2u_0}{\pi^2} & \frac{\hbar^2}{2m}\frac{9\pi^2}{a^2} - \frac{u_0(9\pi^2+4)}{18\pi^2} - E \end{pmatrix}\begin{pmatrix} c_1 \\ c_3 \end{pmatrix} = 0$$

SQ12

To have non-trivial solution (i.e. $C_1 \neq 0$ and $C_2 \neq 0$), we have

$$\begin{vmatrix} \frac{\hbar^2}{2m}\frac{\pi^2}{a^2} - \frac{U_0(\pi^2+4)}{2\pi^2} - E & \frac{2U_0}{\pi^2} \\ \frac{2U_0}{\pi^2} & \frac{\hbar^2}{2m}\frac{9\pi^2}{a^2} - \frac{U_0(9\pi^2+4)}{18\pi^2} - E \end{vmatrix} = 0$$

$$\left[\frac{\hbar^2}{2m}\frac{\pi^2}{a^2} - \frac{U_0(\pi^2+4)}{2\pi^2} - E\right]\left[\frac{\hbar^2}{2m}\frac{9\pi^2}{a^2} - \frac{U_0(9\pi^2+4)}{18\pi^2} - E\right] - \frac{4U_0^2}{\pi^4} = 0$$

$$E = \frac{5\hbar^2\pi^2}{2ma^2} - \frac{U_0(9\pi^2+20)}{18\pi^2} \pm \sqrt{\frac{4\hbar^4\pi^4}{m^2a^4} + \frac{32}{9}\frac{\hbar^2 U_0}{ma^2} + \frac{388}{81}\frac{U_0^2}{\pi^4}}$$

The lower one is an estimate to E_{GS}

$$\langle \hat{H} \rangle_{\phi,\min} = \frac{5\hbar^2\pi^2}{2ma^2} - \frac{U_0(9\pi^2+20)}{18\pi^2} - \sqrt{\frac{4\hbar^4\pi^4}{m^2a^4} + \frac{32}{9}\frac{\hbar^2 U_0}{ma^2} + \frac{388}{81}\frac{U_0^2}{\pi^4}}$$

$$= \frac{5\hbar^2\pi^2}{2ma^2} - \frac{U_0(9\pi^2+20)}{18\pi^2} - \frac{2\hbar^2\pi^2}{ma^2}\sqrt{1 + \frac{8U_0ma^2}{9\hbar^2\pi^4} + \frac{97U_0^2m^2a^4}{81\hbar^4\pi^8}}$$

Remarks :

1) When $U_0 = 0$, $\langle \hat{H} \rangle_{\phi,\min} = \frac{\pi^2\hbar^2}{2ma^2}$ which is the GS Energy of 1D infinite well. It should be expected!