# CAS PY 452

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Discussion Notes
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## Variational method for the hydrogen atom

**Problem statement:** The hydrogen atom Hamiltonian is,

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}, \tag{1}$$

where we have used the approximation $m_{\text{nucleus}} \gg m_e$, where $m_e$ is the mass of the electron. Use the following two ansatzes in order to estimate the ground state wavefunction and the ground state energy using the variational method:

$$\psi_e(r,\theta,\phi) = Ae^{-r/a} \tag{2}$$

$$\psi_g(r,\theta,\phi) = Be^{-(r/a)^2}, \tag{3}$$

where $A, B$ are normalization constants.

**Solution:** First, we find the normalization constants by using integration by parts twice. The relevant product rule calculations are,

$$-\frac{a}{2}\frac{d}{dr}(e^{-2r/a}r^2) = e^{-2r/a}r^2 - ae^{-2r/a}r. \qquad -\frac{a}{2}\frac{d}{dr}(e^{-2r/a}r) = -\frac{a}{2}e^{-2r/a} + re^{-2r/a} \tag{4}$$

$$\begin{aligned}\iint\int_0^\infty |\psi_e|^2 r^2 \,\mathrm{d}r\,\mathrm{d}\Omega &= 4\pi|A|^2\int_0^\infty e^{-2r/a}r^2\,\mathrm{d}r = 4\pi|A|^2\left(-\frac{a}{2}e^{-2r/a}r^2\Big|_{r=0}^{r\to\infty} + a\int_0^\infty e^{-2r/a}r\,\mathrm{d}r\right)\\ &= 4\pi|A|^2\left(0 + a\left[-\frac{a}{2}e^{-2r/a}r\Big|_{r=0}^{r\to\infty} + \frac{a}{2}\int_0^\infty e^{-2r/a}\,\mathrm{d}r\right]\right) = 4\pi|A|^2\frac{a^2}{2}\frac{a}{2} = \pi|A|^2a^3\end{aligned} \tag{5}$$

$$\pi|A|^2a^3 = 1 \implies A = \frac{1}{\sqrt{a^3\pi}} \tag{6}$$

$$-\frac{a^2}{4}\frac{d}{dr}(re^{-2(r/a)^2}) = r^2e^{-2(r/a)^2} - \frac{a^2}{4}e^{-2(r/a)^2} \tag{7}$$

$$\begin{aligned}\iint\int_0^\infty |\psi_g|^2 r^2\,\mathrm{d}r\,\mathrm{d}\Omega &= 4\pi|B|^2\int_0^\infty e^{-2(r/a)^2}r^2\,\mathrm{d}r = 4\pi|B|^2\times\frac{a^2}{4}\left(-re^{-2(r/a)^2}\Big|_{r=0}^{r\to\infty} + \int_0^\infty e^{-2(r/a)^2}\,\mathrm{d}r\right)\\ &= \pi a^2|B|^2\left(-0 + \frac{1}{2}\times\frac{a}{\sqrt{2}}\int_{-\infty}^\infty e^{-u^2}du\right) = a^3|B|^2(\pi/2)^{3/2}\end{aligned} \tag{8}$$

$$a^3|B|^2(\pi/2)^{3/2} = 1 \implies B = \left(\frac{2}{\pi a^2}\right)^{3/4} \tag{9}$$

The variational method lets us find an upper bound on the ground state energy and an approximate ground state wave-function by minimizing the energy functional $\langle\psi|\hat{H}|\psi\rangle$ over states $|\psi\rangle$. To compute the energy functional, we act on our ansatz states $\psi_e, \psi_g$ with the Hamiltonian. First recall that the spherical Laplacian when acting on a function with no angular dependence is,

$$\nabla^2 f(r) = \frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r}, \tag{10}$$

so we find:

$$\hat{H}[\psi_e]/A = -\frac{\hbar^2}{2m_e}\left(\frac{1}{a^2}e^{-r/a} - \frac{2}{ar}e^{-r/a}\right) - \frac{e^2}{4\pi\epsilon_0 r}e^{-r/a} = -\frac{\hbar^2}{2ma^2}e^{-r/a} + \left(\frac{\hbar^2}{ma} - \frac{e^2}{4\pi\epsilon_0}\right)\frac{e^{-r/a}}{r} \tag{11}$$

$$\hat{H}[\psi_g]/B = -\frac{\hbar^2}{2m_e}\left(\frac{4r^2}{a^4}e^{-(r/a)^2} - \frac{6}{a^2}e^{-(r/a)^2}\right) - \frac{e^2}{4\pi\epsilon_0 r}e^{-(r/a)^2} = \frac{3\hbar^2}{ma^2}e^{-(r/a)^2} - \frac{2\hbar^2}{ma^4}r^2e^{-(r/a)^2} - \frac{e^2}{4\pi\epsilon_0}\frac{e^{-(r/a)^2}}{r} \tag{12}$$

Next, we compute the inner products:

$$\begin{aligned}\langle\psi_e|\hat{H}|\psi_e\rangle &= \iint\int_0^\infty \psi_e^*\hat{H}[\psi_e]r^2\,\mathrm{d}r\,\mathrm{d}\Omega = 4\pi A^2\left[-\frac{\hbar^2}{2ma^2}\int_0^\infty r^2e^{-2r/a}\,\mathrm{d}r + \left(\frac{\hbar^2}{ma} - \frac{e^2}{4\pi\epsilon_0}\right)\int_0^\infty r^2\frac{e^{-2r/a}}{r}\,\mathrm{d}r\right]\\
&= 4\pi A^2\left[-\frac{\hbar^2}{2ma^2}\left(-\frac{a}{2}r^2e^{-2r/a}\Big|_{r=0}^{r\to\infty} + a\times\frac{a}{2}\left(-re^{-2r/a}\Big|_{r=0}^{r\to\infty} + \int_0^\infty e^{-2r/a}\,\mathrm{d}r\right)\right)\right.\\
&\quad\left. + \left(\frac{\hbar^2}{ma} - \frac{e^2}{4\pi\epsilon_0}\right)\frac{a}{2}\left(-re^{-2r/a}\Big|_{r=0}^{r\to\infty} + \int_0^\infty e^{-2r/a}\,\mathrm{d}r\right)\right] = 4\pi A^2\left[-\frac{\hbar^2}{2m}\times\frac{a}{4} + \left(\frac{\hbar^2}{ma} - \frac{e^2}{4\pi\epsilon_0}\right)\frac{a^2}{4}\right]\\
&= \frac{\hbar^2}{2m}a^{-2} - \frac{e^2}{4\pi\epsilon_0}a^{-1}.\end{aligned} \tag{13}$$

$$\begin{aligned}\langle\psi_g|\hat{H}|\psi_g\rangle &= \iint\int_0^\infty \psi_g^*\hat{H}[\psi_g]r^2\,\mathrm{d}r\,\mathrm{d}\Omega = 4\pi B^2\left[\frac{3\hbar^2}{ma^2}\int_0^\infty r^2e^{-2(r/a)^2}\,\mathrm{d}r - \frac{2\hbar^2}{ma^4}\int_0^\infty r^4e^{-2(r/a)^2}\,\mathrm{d}r - \frac{e^2}{4\pi\epsilon_0}\int_0^\infty re^{-2(r/a)^2}\,\mathrm{d}r\right]\\
&= \frac{8}{a^3}\sqrt{\frac{2}{\pi}}\left[\frac{3\hbar^2}{ma^2}\times\frac{a^3}{8}\sqrt{\frac{\pi}{2}} - \frac{2\hbar^2}{ma^4}\times\frac{3a^5}{32}\sqrt{\frac{\pi}{2}} - \frac{e^2}{4\pi\epsilon_0}\times\frac{a^2}{4}\right] = \frac{3\hbar^2}{2m}a^{-2} - \frac{e^2}{\sqrt{2\pi^3}\epsilon_0}a^{-1}.\end{aligned} \tag{14}$$

To compute the inner product for $\psi_g$, we used integration by parts following from the product rule,

$$-\frac{a^2}{4}\frac{d}{dr}(r^3e^{-2(r/a)^2}) = r^4e^{-2(r/a)^2} - \frac{3a^2}{4}r^2e^{-2(r/a)^2} \tag{15}$$

to compute the following integrals:

$$\int_0^\infty r^2e^{-2(r/a)^2}\,\mathrm{d}r = -\frac{a^2}{4}re^{-2(r/a)^2}\Big|_{r=0}^{r\to\infty} + \frac{a^2}{4}\int_0^\infty e^{-2(r/a)^2} = 0 + \frac{a^3}{8\sqrt{2}}\int_{-\infty}^\infty e^{-u^2}\,\mathrm{d}u = \frac{a^3}{8}\sqrt{\frac{\pi}{2}}, \tag{16}$$

$$\int_0^\infty r^4e^{-2(r/a)^2}\,\mathrm{d}r = -\frac{a^2}{4}r^3e^{-2(r/a)^2}\Big|_{r=0}^{r\to\infty} + \frac{3a^2}{4}\int_0^\infty r^2e^{-2(r/a)^2}\,\mathrm{d}r = 0 + \frac{3a^2}{4}\times\frac{a^3}{8}\sqrt{\frac{\pi}{2}} = \frac{3a^5}{32}\sqrt{\frac{\pi}{2}}, \tag{17}$$

$$\int_0^\infty re^{-2(r/a)^2}\,\mathrm{d}r = \frac{a^2}{4}\int_0^\infty e^{-u}\,\mathrm{d}u = \frac{a^2}{4}. \tag{18}$$

Our variational parameter is $a$, so we must minimize these inner products (lines 14 and 13). We will minimize these by finding stationary points:

$$\frac{\partial}{\partial a}\langle\psi_e|\hat{H}|\psi_e\rangle = -\frac{\hbar^2}{m}a^{-3} + \frac{e^2}{4\pi\epsilon_0}a^{-2} = 0 \implies a_e^\star = \frac{4\pi\epsilon_0\hbar^2}{e^2m} = 52.918\,\mathrm{pm}, \tag{19}$$

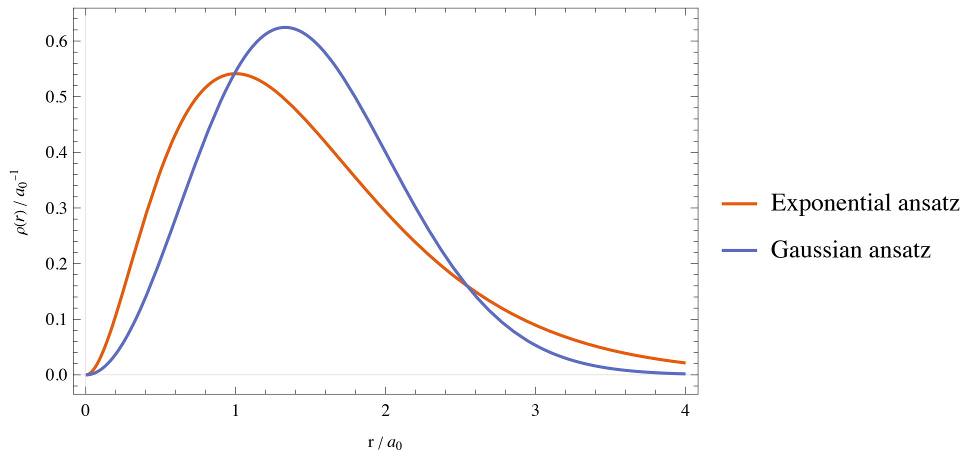
$$\frac{\partial}{\partial a}\langle\psi_g|\hat{H}|\psi_g\rangle = -\frac{3\hbar^2}{m}a^{-3} + \frac{e^2}{\sqrt{2}\pi^{3/2}\epsilon_0}a^{-2} = 0 \implies a_g^\star = \frac{3\sqrt{2}\pi^{3/2}\hbar^2\epsilon_0}{e^2m} = 99.484\,\mathrm{pm}. \tag{20}$$

Observe that $a_e^\star$, the variational parameter that minimizes $\langle\psi_e|\hat{H}|\psi_e\rangle$ for the ansatz $\psi_e$, is exactly the Bohr radius! Using the calculations done in the appendix, according to the ansatz $\psi_e$, there is a 50% probability the electron will be a distance 70.753 pm or less from the nucleus, and according to the ansatz $\psi_g$, there is a 50% probability the electron will be a distance 76.512 pm from the nucleus. Therefore, the variational method applied to the exponential ansatz describes a wave-function concentrated closer to the origin compared to the Gaussian ansatz. Substituting the variational parameters $a_e^\star$ and $a_g^\star$ into the inner products (lines 13 and 14), we get,

$$\langle\psi_e|\hat{H}|\psi_e\rangle\Big|_{a=a_e^\star} = -\frac{e^4m}{32\pi^2\hbar^2\epsilon_0} = -13.61\,\mathrm{eV} \tag{21}$$

$$\langle\psi_g|\hat{H}|\psi_g\rangle\Big|_{a=a_g^\star} = -\frac{e^4m}{12\pi^3\hbar^2\epsilon_0} = -11.55\,\mathrm{eV}. \tag{22}$$

These are the variational energies resulting from the ansatzes $\psi_e$ and $\psi_g$, respectively. Because the variational energy for the Gaussian ansatz is greater than the variational energy for the exponential ansatz, we immediately know that the Gaussian ansatz is incorrect. Additionally, we see that the variational energy found for the exponential ansatz is exactly the energy of the ground state of hydrogen found by solving analytically.




### Appendix: calculating 50th percentile

$$4\pi \int_0^x r^2 |\psi_e|^2 \, \mathrm{d}r = 4\pi A^2 \int_0^x r^2 e^{-2(r/a_e^\star)} \, \mathrm{d}r = 1 - e^{-2x/a_e^\star} \left(1 + \frac{2x}{a_e^\star} + \frac{2x^2}{a_e^{\star 2}}\right) = \frac{1}{2} \implies x_{50} = 1.337 a_e^\star. \tag{23}$$

$$4\pi \int_0^x r^2 |\psi_g|^2 \, \mathrm{d}r = 4\pi B^2 \int_0^x r^2 e^{-2(r/a_g^\star)^2} \, \mathrm{d}r = \mathrm{erf}\left(\frac{\sqrt{2}x}{a_g^\star}\right) - \frac{2x}{a_g^\star}\sqrt{\frac{2}{\pi}} e^{-2(x/a_g^\star)^2} \implies x_{50} = 0.7691 a_g^\star \tag{24}$$

The relations between $x_{50}$ and $a^\star$ are found by converting to dimensionless units $x_{50}/a^\star$ and solving numerically.