Quantum Mechanics II
HW 1

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1. Consider the 1-dimensional double-well Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{8a^2}(x^2 - a^2)^2$$

(a) Show that an expansion about either one of the wells, in the limit of large separation between the wells, leads to a harmonic oscillator system of frequency ω.

First, we expand the potential V about a

$$V = \frac{m\omega^2}{2}\left[(x-a)^2 + \frac{(x-a)^3}{a} + \frac{(x-a)^4}{4a^2}\right].$$

In the limit of large separation between wells, we see that the last two terms tend toward zero for x in the neighborhood of a. This leaves us with a Hamiltonian of

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

which represents the Hamiltonian of a harmonic oscillator centered around a. A similar result applies if we instead expand about $-a$.

(b) Make an educated guess for the form of the wavefunction for the ground state and first excited state, in the limit of large separation between the wells.

Based on part (a), we see that for large separation between wells the potential takes the form of two harmonic oscillators; one at a and one at $-a$. As such, a reasonable guess for a ground state wave function would be two Gaussians centered at both a and $-a$. As our potential is even, both even and odd solutions are permitted. Since the ground state is symmetric, we guess a solution of

$$|\Psi_0\rangle = \langle x-a|0\rangle + \langle x+a|0\rangle$$

where $\langle x|n\rangle$ represents the nth state of the harmonic oscillator. The next excited state will be an antisymmetric combination of the two Gaussians

$$|\Psi_1\rangle = \langle x-a|0\rangle - \langle x+a|0\rangle.$$

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(c) For each of these two wavefunctions, compute $\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$

First, for the approximate ground state energy (not yet taking the limit of large well separation) we have

$$\langle \Psi_0 | H | \Psi_0 \rangle = \int_{-\infty}^{\infty} \Psi_0(x) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m\omega^2}{2} (x^2 - a^2)^2 \right) \Psi_0(x) \, dx$$

where

$$\Psi_0(x) = \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} \exp\left[-\frac{m\omega}{2\hbar} (x-a)^2 \right] + \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} \exp\left[-\frac{m\omega}{2\hbar} (x+a)^2 \right].$$

Evaluating the integral we find

$$\langle \Psi_0 | H | \Psi_0 \rangle = \hbar\omega + \frac{3}{16} \frac{\hbar^2}{a^2 m} + \exp\left(-\frac{a^2 m\omega}{\hbar} \right) \left[\frac{1}{4} \frac{\hbar}{\omega} + \frac{3}{16} \frac{\hbar^2}{a^2 m} - \frac{3}{4} a^2 m\omega^2 \right]$$

with norm squared

$$\langle \Psi_0 | \Psi_0 \rangle = 2 + 2\exp\left(\frac{a^2 m\omega}{\hbar} \right).$$

Dividing the two, we arrive at our estimation of the ground state energy

$$\frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = \frac{\hbar\omega}{2} \left[1 + \frac{3}{16} \frac{\hbar}{a^2 m\omega} - \frac{3}{4} \left(\frac{a^2 m\omega}{\hbar} + 1 \right) \frac{1}{1 + \exp\left(\frac{a^2 m\omega}{\hbar} \right)} \right]. \qquad (1)$$

For the first excited state, the relevant quantities are

$$\Psi_1(x) = \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} \exp\left[-\frac{m\omega}{2\hbar} (x-a)^2 \right] - \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} \exp\left[-\frac{m\omega}{2\hbar} (x+a)^2 \right]$$

$$\langle \Psi_1 | H | \Psi_1 \rangle = \hbar\omega + \frac{3}{16} \frac{\hbar^2}{a^2 m} - \exp\left(-\frac{a^2 m\omega}{\hbar} \right) \left[\frac{1}{4} \frac{\hbar}{\omega} + \frac{3}{16} \frac{\hbar^2}{a^2 m} - \frac{3}{4} a^2 m\omega^2 \right]$$

$$\langle \Psi_1 | \Psi_1 \rangle = 2 - 2\exp\left(\frac{a^2 m\omega}{\hbar} \right)$$

thus

$$\frac{\langle \Psi_1 | H | \Psi_1 \rangle}{\langle \Psi_1 | \Psi_1 \rangle} = \frac{\hbar\omega}{2} \left[1 + \frac{3}{16} \frac{\hbar}{a^2 m\omega} + \frac{3}{4} \left(\frac{a^2 m\omega}{\hbar} + 1 \right) \frac{1}{\exp\left(\frac{a^2 m\omega}{\hbar} \right) - 1} \right]. \qquad (2)$$

(d) Deduce that in the limit of large separation between the wells the energies are approximately:

$$E_0 \approx \frac{\hbar\omega}{2} \left[1 + \frac{3}{16} \frac{\hbar}{a^2 m\omega} - \frac{3}{4} \frac{a^2 m\omega}{\hbar} \exp\left[-\frac{a^2 m\omega}{\hbar} \right] + ... \right]$$

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$$E_1 \approx \frac{\hbar\omega}{2}\left[1 + \frac{3}{16}\frac{\hbar}{a^2 m\omega} + \frac{3}{4}\frac{a^2 m\omega}{\hbar}\exp\left[-\frac{a^2 m\omega}{\hbar}\right] + \dots\right]$$

Thus, the energy splitting is exponentially small in the limit of large separation between the wells.

In the limit of large separation between wells

$$\exp\left(\frac{a^2 m\omega}{\hbar}\right) \gg 1$$

such that (1) and (2) respectively become

$$E_0 \approx \frac{\hbar\omega}{2}\left[1 + \frac{3}{16}\frac{\hbar}{a^2 m\omega} - \frac{3}{4}\frac{a^2 m\omega}{\hbar}\exp\left[-\frac{a^2 m\omega}{\hbar}\right] - \frac{3}{4}\exp\left[-\frac{a^2 m\omega}{\hbar}\right]\right]$$

$$E_1 \approx \frac{\hbar\omega}{2}\left[1 + \frac{3}{16}\frac{\hbar}{a^2 m\omega} + \frac{3}{4}\frac{a^2 m\omega}{\hbar}\exp\left[-\frac{a^2 m\omega}{\hbar}\right] + \frac{3}{4}\exp\left[-\frac{a^2 m\omega}{\hbar}\right]\right].$$

2. Evaluate the integrals involved in the derivation of the variational approximation for the ground state energy of He. Specifically, evaluate the integrals involved in going from the first line to the second line of the formula (16.1.15) in Shankar.

If we ignore the electron-electron repulsion we see that the helium Hamiltonian resembles that of two hydrogen Hamiltonians with $Z = 2$. Trying a wavefunction of the product of two $Z = 2$ hydrogen ground states in the full helium hamiltonian, we find that the ground state energy is about -75eV. The actual energy of ground state of the He atom is -78.6eV. To better our approximation, we allow Z to be a free parameter. The motivation is that the effective potential each electron sees will be slightly less than $Z = 2$, due to the electron screening. As such, we will guess a solution of the ground state wavefunction as

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a_0^3}\exp\left[\frac{-Z(r_1 + r_2)}{a_0}\right]$$

and we may express our (unchanged) Hamiltonian as

$$H = \left[-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}\right] + \frac{(Z-2)e^2}{r_1} + \frac{(Z-2)e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

In evaluating $\langle\psi|H|\psi\rangle$ we see that the bracketed term in our Hamiltonian is just twice the energy of the $Z = 2$ hydrogen-like atom. Thus

$$\langle\psi|H|\psi\rangle = \langle\psi|H_0|\psi\rangle + \langle\psi|G + I|\psi\rangle$$

$$= -Z^2\frac{e^2}{a_0} + \langle\psi|G + I|\psi\rangle.$$

where we have separated the remaining Hamiltonian into two parts

$$I \equiv \langle\psi|\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}|\psi\rangle$$

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$$G \equiv \langle \psi | \frac{(Z-2)e^2}{r_1} + \frac{(Z-2)e^2}{r_2} | \psi \rangle.$$

Evaluating G first (as ψ is real, we omit complex conjugates in inner products)

$$G = \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \, \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)\frac{(Z-2)e^2}{r_1}\psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$$
$$+ \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \, \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)\frac{(Z-2)e^2}{r_2}\psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$$

where $\psi_{100}(\mathbf{x})$ represents the ground state of the Z hydrogen-like atom. Working on the first integral above we have

$$\int d^3\mathbf{r}_1 \, \psi_{100}(\mathbf{r}_1)\frac{(Z-2)e^2}{r_1}\psi_{100}(\mathbf{r}_1) \int d^3\mathbf{r}_2 \, \psi_{100}(\mathbf{r}_2)\psi_{100}(\mathbf{r}_2)$$
$$= \int d^3\mathbf{r}_1 \, \psi_{100}(\mathbf{r}_1)\frac{(Z-2)e^2}{r_1}\psi_{100}(\mathbf{r}_1)$$
$$= (Z-2)e^2\frac{4\pi Z^3}{\pi a_0^3}\int_0^\infty dr_1 \, \exp\left[\frac{-2Zr_1}{a_0}\right]r_1$$
$$= (Z-2)e^2\frac{Z}{a_0}.$$

We can see that the second integral in G is in fact the same integral, thus

$$G = 2(Z-2)e^2\frac{Z}{a_0}.$$

For the interaction integral I, we need to compute

$$I = \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \, \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$$
$$= e^2 \int d^3\mathbf{r}_2 \, \psi_{100}^2(\mathbf{r}_2) \int d^3\mathbf{r}_1 \, \psi_{100}^2(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Looking at the second integral, the potential can be expanded in terms of Legendre polynomials as

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_l \frac{r_1^l}{r_2^{l+1}}P_l(\cos\theta) \quad r_1 < r_2.$$

If we orient $\mathbf{r}_2$ to lie along the z-axis, we may express the integral as

$$2\pi\frac{Z^3}{\pi a_0^3}\int_0^\pi \int_0^{r_2} d\theta \, dr_1 \, r_1^2 \sin\theta \left(\sum_l \frac{r_1^l}{r_2^{l+1}}P_l(\cos\theta)\right)\exp\left[\frac{-2Zr_1}{a_0}\right]$$
$$+ 2\pi\frac{Z^3}{\pi a_0^3}\int_0^\pi \int_{r_2}^\infty d\theta \, dr_1 \, r_1^2 \sin\theta \left(\sum_l \frac{r_2^l}{r_1^{l+1}}P_l(\cos\theta)\right)\exp\left[\frac{-2Zr_1}{a_0}\right].$$

If we look at the orthonormality of the Legendre polynomials

$$\int_0^\pi d\theta \, P_l(\cos\theta)P_m(\cos\theta) = \frac{2}{2l+1}\delta_{lm}$$

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and note that $P_0(\cos\theta) = 1$, we observe that only the $l = 0$ term will survive in each integral. Thus

$$\int d^3\mathbf{r}_1\, \psi_{100}^2(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{4Z^3}{a_0^3}\left(\int_0^{r_2} dr_1\, \frac{r_1^2}{r_2}\exp\left[\frac{-2Zr_1}{a_0}\right] + \int_{r_2}^\infty dr_1\, r_1\exp\left[\frac{-2Zr_1}{a_0}\right]\right)$$

$$= \frac{1}{r_2} - \left(\frac{1}{r_2} + \frac{Z}{a_0}\right)\exp\left(\frac{-2Zr_2}{a_0}\right).$$

Lastly, we integrate with respect to to $\mathbf{r}_2$

$$I = e^2\left(\frac{4Z^3}{a_0^3}\right)\int_0^\infty dr_2\, r_2^2\exp\left[\frac{-2Zr_2}{a_0}\right]\left[\frac{1}{r_2} - \left(\frac{1}{r_2} + \frac{Z}{a_0}\right)\exp\left(\frac{-2Zr_2}{a_0}\right)\right]$$

$$= \frac{5}{8}\frac{Ze^2}{a_0}$$

Altogether we have

$$\langle\psi|H|\psi\rangle = -Z^2\frac{e^2}{a_0} + 2Z(Z-2)\frac{e^2}{a_0} + \frac{5}{8}\frac{Ze^2}{a_0}.$$

Substituting

$$\mathrm{Ry} = \frac{e^2}{2a_0}$$

we can express the approximate ground state energy of Helium as

$$\langle\psi|H|\psi\rangle = -2\mathrm{Ry}\left[4Z - Z^2 - \frac{5}{8}Z\right]$$

3. Consider the hydrogen molecule ion problem with Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2}$$

where r_1 and r_2 are the distances of the electron from each nucleus, R is the separation between the two nuclei. Thus, with one nucleus at the origin and the other on the z-axis at $z = R$, we have in terms of spherical polar coordinates: $r_1 = r$, and $r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta}$, where θ is the angle to the z-axis.

For the ground and first-excited states choose trial wavefunction

$$\psi_\pm = A(\psi_0(r_1) \pm \psi_0(r_2))$$

where $\psi_0(r)$ is the normalized ground state wavefunction of hydrogen.

(a) Show that the overlap integral is

$$I \equiv \langle \psi_0(r_1)|\psi_0(r_2)\rangle = \left[1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right]e^{-R/a}$$

where a is the Bohr radius.

The normalized ground state wavefunction for hydrogen is

$$\psi_0(r) = \sqrt{\frac{1}{\pi a^3}}e^{-r/a}.$$

Substituting the relevant quantities into the overlap integral we have

$$I = \frac{1}{\pi a^3}\int\limits_0^{2\pi}\int\limits_0^\pi\int\limits_0^\infty d\phi\, d\theta\, dr\, r^2 \sin\theta\, \exp\left[-\frac{r}{a}\right]\exp\left[-\frac{\sqrt{r^2 + R^2 - 2rR\cos\theta}}{a}\right]$$

$$= \frac{2}{a^3}\int_0^\pi\int_0^\infty dr\, d\theta\, r^2 \sin\theta\exp\left[-\frac{r}{a}\right]\exp\left[-\frac{\sqrt{r^2 + R^2 - 2rR\cos\theta}}{a}\right]$$

$$= \frac{4}{a^3}\left(e^{-R/a}\left[\frac{a^3}{4} + \frac{1}{4}Ra^2 + \frac{1}{12}R^2a\right]\right)$$

$$= \left[1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right]e^{-R/a}$$

(b) Show that the direct integral is

$$D \equiv a\,\langle\psi_0(r_1)|\frac{1}{r_2}|\psi_0(r_1)\rangle = \frac{a}{R} - \left(1 + \frac{a}{R}\right)e^{-2R/a}$$

For the direct integral we have

$$D = \frac{2}{a^2}\int_0^\pi\int_0^\infty d\theta\, dr\, r^2 \sin\theta\frac{e^{-\frac{2r}{a}}}{\sqrt{r^2 + R^2 - 2rR\cos\theta}}.$$

For the angular part

$$\int_0^\pi d\theta\,\frac{\sin\theta}{\sqrt{r^2 + R^2 - 2rR\cos\theta}} = \frac{1}{rR}\sqrt{r^2 + R^2 - 2rR\cos\theta}\Big|_0^\pi$$

$$= \frac{1}{rR}\left[(r + R) - |r - R|\right].$$

Incorporating the absolute value, we now integrate over the radius

$$D = \frac{2}{a^2}\left[\int_0^R dr\left(\frac{2}{R}\right)r^2 e^{-\frac{2r}{a}} + \int_R^\infty dr\, 2r\, e^{-\frac{2r}{a}}\right]$$

$$= \frac{a}{R} - \left(1 + \frac{a}{R}\right)e^{-2R/a}$$

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(c) Show that the exchange integral is

$$X \equiv a \, \langle \psi_0(r_1) | \frac{1}{r_1} | \psi_0(r_2) \rangle = \left(1 + \frac{R}{a}\right) e^{-R/a}$$

Now for the exchange integral

$$X = \frac{2}{a^2} \int_0^\pi \int_0^\infty dr \, d\theta \, r \exp\left[-\frac{r}{a}\right] \exp\left[-\frac{\sqrt{r^2 + R^2 - 2rR\cos\theta}}{a}\right].$$

This is very similar to the overlap integral with a linear factor of r in the integrand. Thus

$$X = \frac{2}{a^2} \int_0^\pi \int_0^\infty dr \, d\theta \, r \exp\left[-\frac{r}{a}\right] \exp\left[-\frac{\sqrt{r^2 + R^2 - 2rR\cos\theta}}{a}\right]$$

$$= \left(1 + \frac{R}{a}\right) e^{-R/a}$$

(d) Hence, including the nucleus-nucleus electrostatic energy $\frac{e^2}{R}$, show that the total energy expectation value for $\psi_\pm$ can be written as

$$\frac{\langle \psi\pm | H_{total} | \psi\pm \rangle}{\langle \psi\pm | \psi\pm \rangle} = |E_{Bohr}| \left\{ -1 + 2\frac{a}{R} \left[\frac{\left(1 + \frac{R}{a}\right) e^{-2R/a} \pm \left(1 - \frac{2}{3}\left(\frac{R}{a}\right)^2\right) e^{-R/a}}{1 \pm \left(1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right) e^{-R/a}} \right] \right\}$$

Let's start with the ground state wavefunction

$$\psi_+ = A \left[\psi_0(r_1) + \psi_0(r_2)\right].$$

We will denote this state as

$$|\psi_+\rangle = A \left(|\psi_{01}\rangle + |\psi_{02}\rangle\right)$$

such that $\langle r_1 | \psi_{01} \rangle = \psi_0(r_1)$ and $\langle r_2 | \psi_{02} \rangle = \psi_0(r_2)$.
For the normalization

$$\langle \psi_+ | \psi_+ \rangle = A^2 \left(1 + 1 + 2 \langle \psi_{01} | \psi_{02} \rangle\right)$$

$$= 2A^2 (1 + I)$$

$$= 2A^2 \left(1 + \left[1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right] e^{-R/a}\right)$$

Now for the Hamiltonian

$$\langle \psi_+ | H | \psi_+ \rangle = A^2 \left(\langle \psi_{01}| + \langle \psi_{02}| \right) | -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} | \left(|\psi_{01}\rangle + |\psi_{02}\rangle\right)$$

$$= A^2 \left[2E_{Bohr} + 2E_{Bohr}I + 4E_{Bohr}(D + X)\right]$$

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$$= 2A^2 |E_{Bohr}| \left(-(1+I) - 2(D+X) \right).$$

Dividing by the normalization,

$$\frac{\langle \psi_+ | H | \psi_+ \rangle}{\langle \psi_+ | \psi_+ \rangle} = |E_{Bohr}| \left\{ -1 - 2\frac{(D+X)}{(1+I)} \right\}$$

$$= |E_{Bohr}| \left\{ -1 + 2\frac{a}{R} \left[\frac{\left(1 + \frac{R}{a}\right) e^{-2R/a} + \left(1 - \frac{2}{3}\left(\frac{R}{a}\right)^2\right) e^{-R/a}}{1 + \left(1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right) e^{-R/a}} \right] \right\}$$

Now for the antisymmetric state

$$|\psi_-\rangle = A \left(|\psi_{01}\rangle - |\psi_{02}\rangle \right)$$

we may use the same I, D, and X integrals to form the expectation of energy as

$$\langle \psi_- | H | \psi_- \rangle = 2A^2 |E_{Bohr}| \left(-(1-I) - 2(D-X) \right)$$

with normalization

$$\langle \psi_- | \psi_- \rangle = 2A^2(1-I).$$

Consequently we have for the asymmetric state

$$\frac{\langle \psi_- | H | \psi_- \rangle}{\langle \psi_- | \psi_- \rangle} = |E_{Bohr}| \left\{ -1 - 2\frac{(D-X)}{(1-I)} \right\}$$

$$= |E_{Bohr}| \left\{ -1 + 2\frac{a}{R} \left[\frac{\left(1 + \frac{R}{a}\right) e^{-2R/a} - \left(1 - \frac{2}{3}\left(\frac{R}{a}\right)^2\right) e^{-R/a}}{1 - \left(1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right) e^{-R/a}} \right] \right\}$$

Thus we arrive at the expression initially given

$$\frac{\langle \psi \pm | H_{total} | \psi \pm \rangle}{\langle \psi \pm | \psi \pm \rangle} = |E_{Bohr}| \left\{ -1 + 2\frac{a}{R} \left[\frac{\left(1 + \frac{R}{a}\right) e^{-2R/a} \pm \left(1 - \frac{2}{3}\left(\frac{R}{a}\right)^2\right) e^{-R/a}}{1 \pm \left(1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right) e^{-R/a}} \right] \right\}$$

where we should also include the contribution of the potential between protons, which goes as
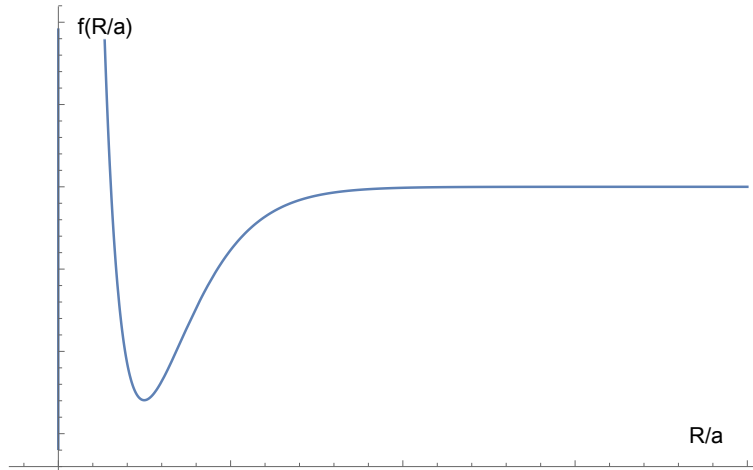
$$\frac{2e^2}{R}(1 \pm I) = |E_{Bohr}|\frac{4a}{R}(1 \pm I)$$

for the ground and first excited state respectively.

(e) Plot these two functions and deduce that the energy expectation value has a minimum for the plus state, but not for the minus state.
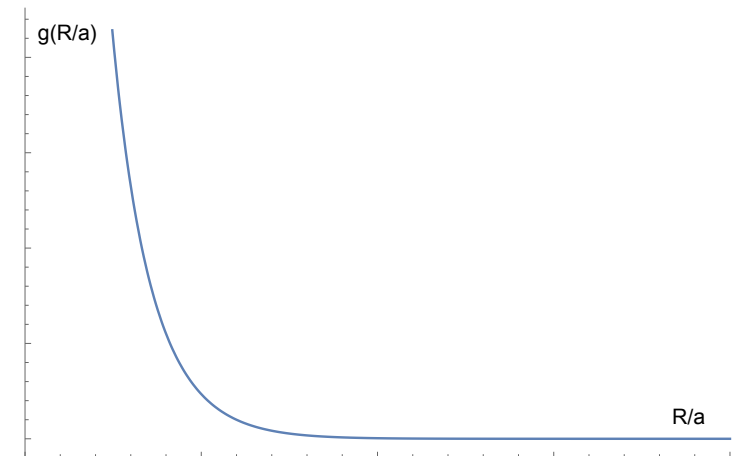
For the ground state we have

$$f(R/a) = \frac{\langle \psi_+ | H | \psi_+ \rangle}{\langle \psi_+ | \psi_+ \rangle}$$

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while for the first excited state we have

$$g(R/a) = \frac{\langle\psi_-|H|\psi_-\rangle}{\langle\psi_-|\psi_-\rangle}$$

As we can see, only the ground state has a minimum for the expectation energy.