

## The Variational Method: HW 3

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1. Compute the variational upper bound for the ground state energy of a particle in the “cut-in-half” linear potential which is given by

$$V(x) = \infty \text{ for } x \leq 0$$
$$V(x) = Bx \text{ for } x > 0$$

using the trial wavefunction

$$\psi(x; \alpha) = A x \exp(-\alpha x).$$

- (a) Calculate the normalization constant  $A$ .
- (b) Calculate the expectation value of the kinetic energy  $\langle T \rangle$ .
- (c) Calculate the expectation value of the potential energy  $\langle V \rangle$ .
- (d) Calculate the expectation value of the total energy  $\langle H \rangle$ .

Find the value of  $\alpha$  that minimizes it.

- (e) Calculate the variational upper bound for the ground state energy.

When  $C = mg$  this problem is known as the quantum mechanical bouncing ball!

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2. Compute the variational upper bound for the ground state energy of a particle in the “cut-in-half” harmonic oscillator potential which is given by

$$V(x) = \infty \text{ for } x \leq 0$$
$$V(x) = Cx^2 \text{ for } x > 0$$

using the trial wavefunction

$$\psi(x; \beta) = A x \exp(-\beta x^2).$$

- (a) Calculate the normalization constant  $A$ .
- (b) Calculate the expectation value of the kinetic energy  $\langle T \rangle$ .
- (c) Calculate the expectation value of the potential energy  $\langle V \rangle$ .
- (d) Calculate the expectation value of the total energy  $\langle H \rangle$ .

Find the value of  $\beta$  that minimizes it.

- (e) Calculate the variational upper bound for the ground state energy.
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3. Use the variational method to calculate the effective screening charge  $Z_{eff}$ , and the variational bound on the ground state energy for the following atoms with only two electrons: helium, lithium, beryllium, boron, carbon, nitrogen, and oxygen.

- (a) Plot  $Z_{eff}$  versus  $Z$  for these atoms.
- (b) Plot the variational bound on the ground state energy versus  $Z$ .
- (c) For helium, compare your result for the variational upper bound for the ground state energy with the measured value—which is  $E_0 = -79.0$  eV.

See the next two appended pages and also see Griffiths' Section 7.2 about the ground state of the helium atom on pages 261-266.

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4. Compute the variational upper bound for the ground state energy of a particle in the quartic potential which is given by

$$V(x) = Dx^4$$

using the trial wavefunction

$$\psi(x; \gamma) = A \exp(-\gamma^2 x^2).$$

- (a) Calculate the normalization constant  $A$ .
- (b) Calculate the expectation value of the kinetic energy  $\langle T \rangle$ .
- (c) Calculate the expectation value of the potential energy  $\langle V \rangle$ .
- (d) Calculate the expectation value of the total energy  $\langle H \rangle$ .

Find the value of  $\gamma$  that minimizes it.

- (e) Calculate the variational upper bound for the ground state energy.

The following integrals will be useful:

$$\int_{-\infty}^{\infty} \exp(-ax^2) dx = \sqrt{\frac{\pi}{a}}$$
$$\int_{-\infty}^{\infty} x^2 \exp(-ax^2) dx = \frac{1}{2} \sqrt{\frac{\pi}{a^3}}$$
$$\int_{-\infty}^{\infty} x^4 \exp(-ax^2) dx = \frac{3}{4} \sqrt{\frac{\pi}{a^5}}$$

**11.4.** (a) Write the Schrödinger equation for the helium atom. What are the solutions for the ground state if one neglects the interaction between the two electrons? (b) Assume that the electrons perform an electric screening of each other and define  $Z$  as a variational parameter. Use the variation method and find  $\langle H \rangle$  and the screening charge.

(a) We begin by considering the Hamiltonian of the helium atom:

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - Ze^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{r_{12}} \quad (11.4.1)$$

where  $r_{12} = |r_1 - r_2|$ . We transform the Hamiltonian to units in which  $e = \hbar = m = 1$ . In these units the Schrödinger equation becomes

$$\left[ -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - Z \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} \right] \psi(r_1, r_2) = E\psi(r_1, r_2) \quad (11.4.2)$$

If one neglects the term  $e^2/r_{12}$  (the interaction term), the solutions are obtained by separation of variables:

$$\Psi_0(r_1, r_2) = u_1(r_1)u_2(r_2) = \frac{Z^{3/2}}{\pi^{1/2}} e^{-Zr_1} \frac{Z^{3/2}}{\pi^{1/2}} e^{-Zr_2} = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \quad (11.4.3)$$

Note that the factors  $\frac{Z^{3/2}}{\pi^{1/2}} e^{-Zr_1}$  and  $\frac{Z^{3/2}}{\pi^{1/2}} e^{-Zr_2}$  are the ground-state functions of a hydrogen-like atom.

(b) In the presence of another electron, each of the electrons is influenced by a decreased charge from the nucleus. We define  $Z_{\text{eff}} = Z - \sigma$ , where  $\sigma$  is the screening charge. We choose the trial function to be

$$\Psi_\sigma(r_1, r_2) = \frac{(Z - \sigma)^3}{\pi} \exp[-(Z - \sigma)(r_1 + r_2)] \quad (11.4.4)$$

Since

$$H\Psi_\sigma = \left[ -(Z - \sigma)^2 - \frac{\sigma}{r_1} - \frac{\sigma}{r_2} + \frac{1}{r_{12}} \right] \Psi_\sigma \quad (11.4.5)$$

then

$$\begin{aligned} \langle H \rangle &= \frac{\iint \Psi_\sigma^* H \Psi_\sigma d^3r_1 d^3r_2}{\iint \Psi_\sigma^* \Psi_\sigma d^3r_1 d^3r_2} = \iint \left[ -(Z - \sigma)^2 - \frac{\sigma}{r_1} - \frac{\sigma}{r_2} + \frac{1}{r_{12}} \right] \Psi_\sigma^2 d^3r_1 d^3r_2 \\ &= -(Z - \sigma)^2 - 2 \frac{(Z - \sigma)^3}{\pi} \int_0^\infty \frac{\sigma}{r} 4\pi r^2 e^{-(Z - \sigma)r} dr + \frac{(Z - \sigma)^6}{\pi^2} \iint \frac{e^{-2(Z - \sigma)(r_1 + r_2)}}{r_{12}} d^3r_1 d^3r_2 \end{aligned} \quad (11.4.6)$$

or

$$\langle H \rangle = -(Z - \sigma)^2 - \frac{2(Z - \sigma)^3}{\pi} \frac{\pi\sigma}{(Z - \sigma)^2} + \frac{(Z - \sigma)^6}{\pi^2} \iint \frac{e^{-2(Z - \sigma)(r_1 + r_2)}}{r_{12}} d^3r_1 d^3r_2 \quad (11.4.7)$$

We solve the last integral using the expansion of  $1/r_{12}$  by Legendre polynomials (see the Mathematical Appendix):

$$\frac{1}{r_{12}} = \begin{cases} \frac{1}{r_1} \sum_{n=0}^{\infty} \left( \frac{r_1}{r_2} \right)^n P_n(\cos\theta) & 0 \leq r_1 \leq r_2 \\ \frac{1}{r_1} \sum_{n=0}^{\infty} \left( \frac{r_2}{r_1} \right)^n P_n(\cos\theta) & r_2 \leq r_1 < \infty \end{cases} \quad (11.4.8)$$

The only terms that contribute to the integral are the ones with  $n = 0$  (since the exponent that enters the integral depends only on the values of  $r_1$  and  $r_2$ , and not on the angle  $\theta$ ); thus,

$$\begin{aligned} \iint \frac{e^{-2(Z-\sigma)(r_1+r_2)}}{r_{12}} d^3r_1 d^3r_2 &= \int e^{-2(Z-\sigma)r_2} \left[ 4\pi \left( \frac{1}{r_2} \int_0^{r_2} r_1^2 e^{-2(Z-\sigma)r_1} dr_1 + \int_{r_2}^{\infty} r_1 e^{-2(Z-\sigma)r_2} dr_1 \right) \right] d^3r_2 \\ &= \frac{5\pi^2}{8(Z-\sigma)^5} \end{aligned} \quad (11.4.9)$$

Thus, the expression for  $\langle H \rangle$  is

$$\langle H \rangle = -(Z-\sigma)^2 - 2(Z-\sigma)\sigma + \frac{5}{8}(Z-\sigma) \quad (11.4.10)$$

Using the condition  $\frac{d\langle H \rangle}{d\sigma} = 0$  we find  $\sigma_0 = \frac{5}{16}$ , and then  $Z_{\text{eff}} = \frac{27}{16}e$ .

**11.5.** Consider a one-dimensional attraction potential  $V(x)$  such that  $V(x) < 0$  for all  $x$ . Using the variational principle show that such a potential has at least one bound state.

For a particle moving in this potential we may choose the following trial wave function:

$$\psi = \sqrt{\frac{2a}{\pi}} \exp(-ax^2) \quad (11.5.1)$$

Note that the function is normalized to unity. Thus, for the ground-state energy we have

$$E_0 \leq \int_{-\infty}^{\infty} \psi^* \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi dx \quad (11.5.2)$$

Since  $V(x) < 0$  for all  $x$ , it remains to prove that  $E_0 < 0$ . Substituting the trial function, we find

$$\begin{aligned} E_0 &\leq \sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} \exp(-ax^2) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \exp(-ax^2) dx \\ &= \sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} \left[ \exp(-ax^2) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) (\exp(-ax^2)) + V(x) \exp(-2ax^2) \right] dx \\ &= \sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} \left[ \frac{a\hbar^2}{2m} [1 - 2ax^2] \exp(-2ax^2) + V(x) \exp(-2ax^2) \right] dx \\ &= \frac{a\hbar^2}{2m} - \frac{a\hbar^2}{2m} \sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} 2ax^2 \exp(-2ax^2) dx + \sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} V(x) \exp(-2ax^2) dx \end{aligned} \quad (11.5.3)$$

We define

$$E'_0 = \frac{a\hbar^2}{2m} + \sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} V(x) \exp(-2ax^2) dx \quad (11.5.4)$$

Thus, since the integral  $\sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} 2ax^2 \exp(-2ax^2) dx$  has a positive value,  $E_0 < E'_0$ . Consider now the minimum value of  $E'_0$ :

$$\frac{\partial E'_0}{\partial a} = \frac{\hbar^2}{2m} + \sqrt{\frac{1}{2a\pi}} \int_{-\infty}^{\infty} V(x) \exp(-2ax^2) dx - \sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} 2x^2 V(x) \exp(-2ax^2) dx = 0 \quad (11.5.5)$$

Combining (11.5.4) and (11.5.5) we obtain

$$(E'_0)_{\min} = \sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} \exp(-2ax^2) (1 + 4ax^2) V(x) dx \quad (11.5.6)$$

since  $\exp(-2ax^2)$  and  $(1 + 4ax^2)$  are positive functions and  $V(x)$  is a negative function for all  $x$ ,  $(E'_0)_{\min} < 0$ , and so is  $E_0$ .