Quantum Mechanics II: PHYS 314 (Spring 2021)
Problem Set 7–Solutions.

Overview

In this Problem Set you will explore variational methods and apply them to several physical systems, such as the Coulomb potential and a model of molecular spectra.

Question 1 [Griffiths 8.21] 20pts

If the photon had a nonzero mass ($m_\gamma \neq 0$), the Coulomb potential would be replaced by the **Yukawa potential**,

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0}\frac{e^{-\mu r}}{r},$$

where $\mu = m_\gamma c/\hbar$. With a trial wavefunction of your own devising, estimate the binding energy of a "hydrogen' atom with this potential. Assume $\mu a \ll 1$, and give your answer correct to order $(\mu a)^2$.

Solution 1

We take the wavefunction as

$$\psi = \frac{1}{\sqrt{\pi b^3}}e^{-r/b}.$$

Then, from the Virial theorem for Hydrogen, we have

$$\langle T\rangle = -E_1 = \frac{\hbar^2}{2mb^2}.$$

Now

$$\begin{aligned}\langle V\rangle &= -\frac{e^2}{4\pi\epsilon_0}\frac{4\pi}{\pi b^3}\int_0^\infty e^{-2r/b}\frac{e^{-\mu r}}{r}r^2\mathrm{d}r = -\frac{e^2}{\pi\epsilon_0 b^3}\int_0^\infty e^{-(2/b+\mu)r}r\mathrm{d}r\\ &= -\frac{e^2}{\pi\epsilon_0 b^3}\frac{1}{(\mu+2/b)^2} = -\frac{e^2}{\pi\epsilon_0 4b(1+\mu b/2)^2}.\end{aligned}$$

Thus

$$\langle H\rangle = \langle T\rangle + \langle V\rangle = \frac{\hbar^2}{2mb^2} - \frac{e^2}{\pi\epsilon_0 4b(1+\mu b/2)^2}.$$

We now need the derivative

$$\frac{\partial\langle H\rangle}{\partial b} = -\frac{\hbar^2}{mb^3} + \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{b^2(1+\mu b/2)^2} + \frac{\mu}{b(1+\mu b/2)^3}\right] = -\frac{\hbar^2}{mb^3} + \frac{e^2}{4\pi\epsilon_0}\frac{(1+3\mu b/2)}{(1+\mu b/2)^3}.$$

Setting this derivative equal to zero leads to

$$\frac{\hbar^2}{m}\frac{4\pi\epsilon_0}{e^2} = \frac{b(1+3\mu b/2)}{(1+\mu b/2)^3},$$

which we can rewrite as

$$\frac{b(1+3\mu b/2)}{(1+\mu b/2)^3} = a.$$

To solve this cubic, we assume $\mu a \ll 1$, which implies $\mu b \ll 1$, since for $\mu = 0$, we have $b = a$. Expanding in powers of $\epsilon = \mu b$, we have

$$a \simeq b\left(1+\frac{3\epsilon}{2}\right)\left[1-\frac{3\epsilon}{2}+6\left(\frac{\epsilon}{2}\right)^2\right] \simeq b\left[1-\frac{3\epsilon^2}{4}\right].$$

The ϵ^2 term is already a second-order correction so we can write this as

$$b \simeq \frac{a}{1-3\mu^2 b^2/4} \simeq a\left(1+\frac{3\mu^2 a^2}{4}\right).$$

Then the minimum of the Hamiltonian is, approximately,

$$\begin{aligned}
\langle H\rangle_{\min} &= \frac{\hbar^2}{2ma^2\left(1+3\mu^2a^2/4\right)} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{a\left(1+3\mu^2a^2/4\right)\left(1+\mu a/2\right)^2} \\
&\simeq \frac{\hbar^2}{2ma^2}\left[1-\frac{3\mu^2a^2}{2}\right] - \frac{e^2}{4\pi\epsilon_0}\frac{1}{a}\left[1-\frac{3\mu^2a^2}{4}\right]\left[1-\mu a+\frac{3\mu^2a^2}{4}\right] \\
&= -E_1\left[1-\frac{3\mu^2a^2}{2}\right] + 2E_1\left[1-\mu a+\frac{3\mu^2a^2}{4}-\frac{3\mu^2a^2}{4}\right] \\
&= \boxed{E_1\left[1-2\mu a+\frac{3\mu^2a^2}{2}\right]}.
\end{aligned}$$

Question 2 **15pts**

A particle of mass m and positive charge q, moving in one dimension, is subject to a uniform electric field $E(x) = -E_0$ for $x > 0$ and $E(x) = E_0$ for $x < 0$. Consider a trial wave function $\psi(x) \propto e^{-\alpha|x|}$ and estimate the ground-state energy by minimizing the expectation value of the energy.

Solution 2

First we need to find the normalisation of the wavefunction

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \mathrm{d}x = 2A^2 \int_0^{\infty} e^{-2\alpha x} \mathrm{d}x = \frac{2A^2}{2\alpha}.$$

Requiring this to be equal to unity, we have $A = \sqrt{\alpha}$.

Thus

$$\frac{\mathrm{d}}{\mathrm{d}x}\psi(x) = \begin{cases} 2\sqrt{\alpha}e^{\alpha x} & x < 0 \\ 2\sqrt{\alpha}e^{-\alpha x} & x > 0 \end{cases},$$

and

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) = \sqrt{\alpha}\left[\alpha^2 e^{-\alpha|x|} - 2\alpha\delta(x)e^{-\alpha|x|}\right] = (\alpha^2 - 2\alpha\delta(x))\psi(x).$$

The expectation value of the Hamiltonian is

$$\begin{aligned}
\langle H\rangle &= \int_{-\infty}^{\infty} \psi(x)\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) + qE_0|x|\psi(x)\right]\mathrm{d}x \\
&= \int_{-\infty}^{\infty} \psi(x)\left[-\frac{\hbar^2}{2m}(\alpha^2 - 2\alpha\delta(x)) + qE_0|x|\right]\psi(x)\mathrm{d}x \\
&= \frac{\alpha\hbar^2}{m}\psi^2(0) - \frac{\hbar^2\alpha^2}{2m}2\alpha\int_0^{\infty} e^{-2\alpha x}\mathrm{d}x + qE_0 2\alpha\int_0^{\infty} x\, e^{-2\alpha x}\mathrm{d}x \\
&= \frac{\alpha^2\hbar^2}{m} - \frac{\alpha^2\hbar^2}{2m} + \frac{qE_0}{2\alpha} = \frac{\alpha^2\hbar^2}{2m} + \frac{qE_0}{2\alpha}.
\end{aligned}$$

Now we take the derivative

$$\frac{\mathrm{d}}{\mathrm{d}\alpha}\langle H\rangle = \alpha\frac{\hbar^2}{m} - \frac{qE_0}{2\alpha^2},$$

and set this to zero. The solution is

$$\alpha_0 = \sqrt[3]{\frac{qE_0 m}{2\hbar^2}},$$

so the bound on the ground state energy is

$$\boxed{E_0 \leq \frac{3}{2^{5/3}}\sqrt[3]{\frac{q^2E_0^2\hbar^2}{m}}}.$$

Note that

$$E_0 \leq \frac{\hbar^2}{2m}\left(\frac{qE_0 m}{2\hbar^2}\right)^{2/3} + \frac{qE_0}{2}\left(\frac{2\hbar^2}{qE_0 m}\right)^{1/3}$$

is acceptable as an answer.

Question 3 **15pts**

Molecular spectra calculations often involve the following potential:

$$U(x) = U_0\left(e^{-2\alpha x} - 2e^{-\alpha x}\right).$$

With the trial wavefunction of your own devising, estimate the ground state energy of such a molecule, assuming $U_0 = \alpha^2\hbar^2/(2m)$. To receive full credit please explain why you chose your particular trial wavefunction. As long as your choice of trial wavefunction is reasonable, your grade will not depend on the closeness of your estimate to the actual answer.

Solution 3

The exact solution to this problem, which is referred to as the Morse potential, is known and is given by

$$E_0^{\text{Morse}} = -\frac{U_0}{4}.$$

The trial wavefunction

$$\psi(x) = \begin{cases} A(x - x_0)e^{-\alpha x} & x \geq x_0 \\ 0 & x < x_0 \end{cases},$$

leads to the bound

$$\langle H \rangle = 0.3U_0.$$

However, since we expect the ground state to be a bound state for molecules, the ground state energy must be negative. So this is not a very good bound. *Note*: The steps required to obtain this result are

1. Find the normalisation $A = 2\alpha^{3/2}e^{\alpha x_0}$ from $|\psi(x)|^2 = 1$.
2. Take derivatives of $\psi(x)$.
3. Calculate $\langle H \rangle$, which is given by

$$\langle H \rangle = \frac{\hbar^2\alpha^2}{2m} + \frac{U_0}{8}e^{-2\alpha x_0} - \frac{16U_0}{27}e^{-\alpha x_0}.$$

4. Solve $\partial\langle H \rangle/(\partial x) = 0$ to find $x_0 = \alpha^{-1}\ln(27/64)$.
5. Plug in the value of x_0 that minimises $\langle H \rangle$.

A better trial wavefunction is

$$\psi(x) = \begin{cases} A(x-x_0)e^{-\beta(x-x_0)} & x \geq x_0 \\ 0 & x < x_0 \end{cases} ,$$

which we have to optimise with respect to both β and x_0. The bound is

$$\langle H \rangle = -0.173 U_0.$$

Note: Award full marks if the correct process is chosen (and no mathematical errors are made along the way):

1. Choose reasonable trial wavefunction (note a plane wave is not a reasonable trial wavefunction). For full marks the wavefunction must satisfy:
    - wavefunction vanishes at $x \to \pm\infty$ so that it is normalisable;
    - if piecewise defined (like the trial wavefunctions above), then the wavefunction must be smooth at the boundary (in the example above, the wavefunction is smooth at $x = x_0$).
2. Ensure wavefunction is normalised.
3. Calculate $\langle H \rangle$.
4. Minimize $\langle H \rangle$.