Quantum Physics III (8.06) Spring 2008
Solution Set 7

April 8, 2008

1. **Variational bound on the ground state in a power-like potential (10 points)**

   The trial wave function is

$$\psi(x) = Ae^{-bx^2} \tag{1}$$

   Normalizing the wavefunction we compute

$$1 = \langle\psi|\psi\rangle = A^2 \int_{-\infty}^{\infty} dx e^{-2bx^2} = A^2 \sqrt{\frac{\pi}{2b}} \tag{2}$$

   and therefore

$$A = \left(\frac{2b}{\pi}\right)^{\frac{1}{4}}. \tag{3}$$

   The expectation value of energy for this wave function is

$$\begin{aligned} E(b) = \langle\psi|H|\psi\rangle &= A^2 \int_{-\infty}^{\infty} dx\, e^{-bx^2} \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \lambda x^4\right) e^{-bx^2} \\ &= \sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} dx\, (\frac{\hbar^2}{2m}(2b - 4b^2x^2) + \lambda x^4) e^{-2bx^2} \\ &= \frac{\hbar^2 b}{2m} + \frac{3\lambda}{16b^2}. \end{aligned} \tag{4}$$

   Requiring the derivative of $E(b)$ with respect to b to be zero we find that the minimum of $\langle\psi|H|\psi\rangle$ is reached at

$$b_{\min} = \left(\frac{3m\lambda}{4\hbar^2}\right)^{\frac{1}{3}}, \tag{5}$$

   with the energy at the minimum

$$E_{\min} = \frac{3}{4}\frac{\hbar^2}{m}\left(\frac{3m\lambda}{4\hbar^2}\right)^{\frac{1}{3}}. \tag{6}$$

   The trial wave function $\psi(x)$ is a linear combination of the ground and excited states. Therefore the energy in the ground state cannot be greater than $E_{\min}$.

2. **Variational bound on the excited states (15 points)**

   (a) **(6 points)** A generic wave function ψ can be expanded in terms of energy eigenfunctions

$$|\psi\rangle = \sum_{n\geq 0} c_n |\psi_n\rangle. \tag{7}$$

   where $|\psi_0\rangle = |\psi_{gs}\rangle$ is the ground state and $|\psi_1\rangle$ is the first excited state with energy $E_1 = E_{fe}$. ψ_n $(n > 1)$ are higher excited states with $E_n \geq E_1$. The condition $\langle\psi|\psi_0\rangle = 0$ implies that $c_0 = 0$ and thus $\langle\psi|\psi\rangle = 1$ leads to

$$\sum_{n\geq 1} |c_n|^2 = 1$$

The expectation value of H is

$$\begin{aligned}
\langle\psi|H|\psi\rangle &= \sum_{m,n\geq 1} c_m^* c_n \langle\psi_m|H|\psi_n\rangle \\
&= \sum_{m,n\geq 1} c_m^* c_n \delta_{m,n} E_n \\
&= \sum_{n\geq 1} |c_n|^2 E_n \\
&\geq \sum_{n\geq 1} |c_n|^2 E_1 \\
&= E_1 \sum_{n\geq 1} |c_n|^2 \\
&= E_1 = E_{fe}.
\end{aligned} \tag{8}$$

Q.E.D.

(b) **(7 points)** Since the potential $1/2m\omega^2x^2$ is even, the ground state must also be an even function of x. We know that the first excited state is an odd function of x, therefore we should choose the trial functions to be an odd function of x as well. Therefore choose

$$|\psi\rangle = Axe^{-bx^2} \tag{9}$$

as a set of the trial functions. Since $|\psi\rangle$ is an odd function of x it correctly has a zero overlap with $|\psi_0\rangle$ Normalizing (9) we write

$$\begin{aligned}
1 = \langle\psi|\psi\rangle &= A^2 \int_{-\infty}^{\infty} dx\, x^2 e^{-2bx^2} \\
&= A^2 \sqrt{\frac{\pi}{2^5 b^3}}
\end{aligned} \tag{10}$$

and thus

$$A = \left(\frac{\pi}{2^5 b^3}\right)^{-\frac{1}{4}} \tag{11}$$

The energy expectation value is

$$\begin{aligned}
E(b) = \langle\psi|H|\psi\rangle &= A^2 \int_{-\infty}^{\infty} dx\, xe^{-bx^2} \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega^2 x^2}{2}\right) xe^{-bx^2} \\
&= \sqrt{\frac{2^5 b^3}{\pi}} \int_{-\infty}^{\infty} dx \left(\frac{3\hbar^2 b}{m} x^2 + \left(\frac{m\omega^2}{2} - \frac{2\hbar^2 b^2}{m}\right) x^4\right) e^{-2bx^2} && (12) \\
&= \frac{3\hbar^2 b}{2m} + \frac{3m\omega^2}{8b}. && (13)
\end{aligned}$$

Setting the derivative of $E(b)$ to zero we find that

$$b_{\min} = \frac{m\omega}{2\hbar} \tag{14}$$

with

$$E_{\min} = \frac{3\hbar\omega}{2}. \tag{15}$$

Note that in this case the variational method gave us exact answer for the energy, which comes at no surprise since our set of trial wave functions $\psi \sim x e^{-bx^2}$ includes that for the first excited state of the harmonic oscillator.

(c) **(2 points)** The same set of trial functions as in (b) can be used to get an estimate for the λx^4 potential since it is also an even function of x. Since $|\psi\rangle$ is an odd function of x it has zero overlap with $|\psi_0\rangle$. The normalization constraint $\langle\psi|\psi\rangle = 1$ will determine A in terms of b, thus giving a one-parametric set of trial functions.

3. **Variational bound on the ground state in an exponential potential (20 points)**

(Full credit will be given to answers to this problem that set $\hbar = 1$.)

(a) **(3 points)** The condition that the wave function be normalized yields $1 = \int d^3r\, C^2\, e^{-2\lambda r} = 4\pi C^2 \int dr\, r^2 e^{-2\lambda r}$. Defining $x = 2\lambda r$, we find $1 = 4\pi C^2 (\frac{1}{2\lambda})^3 \int dx\, x^2 e^{-x}$. Using the identity $\int_0^\infty dx\, x^2 e^{-x} = 2$, we find

$$C^2 = \frac{\lambda^3}{\pi}.$$

(b) **(4 points)** Our trial wavefunction has only radial dependence, therefore angular parts in kinetic energy give 0 when they act on the wavefunction. It is sensible to choose an s-wave ansatz, as was given in the problem, since we expect an s-wave ground state for a particle in a spherically symmetric potential. Using the expression given for E (it can be brought into the form given by using $\nabla^2 = \partial^2/\partial r^2 + 2/r\partial/\partial r$, integrating by parts and remembering that $d^3r \propto r^2 dr$). Therefore, the expectation value of the energy in our trial wave function is given by the integral

$$E = 4\pi C^2 \int dr\, r^2 \left[\frac{\hbar^2}{2m}\lambda^2 e^{-2\lambda r} - \alpha e^{-2(\mu+\lambda)r}\right].$$

Evaluating the above integral we obtain:

$$E = \frac{\hbar^2\lambda^2}{2m} - \alpha\left(\frac{\lambda}{\mu+\lambda}\right)^3.$$

(c) **(5 points)** We minimize E with respect to λ:

$$\frac{\partial E}{\partial \lambda} = \frac{\hbar^2\lambda}{m} - 3\alpha\left(\frac{\lambda}{\mu+\lambda}\right)^2 \frac{\mu}{(\mu+\lambda)^2} = 0.$$

This has the obvious solution $\lambda = 0$; the other solutions are found by solving the quartic equation $(\mu+\lambda)^4 - 3\alpha m\lambda\mu/\hbar^2 = 0$. By glancing at the quartic formula, it is easy to see that the quartic equation has no real roots unless $81\alpha m - 256\mu^2\hbar^2 > 0$, or, in other words, only for $\alpha > \frac{256\mu^2\hbar^2}{81m}$ does E have extrema other than at $\lambda = 0$. Therefore for small α, minimum value of $E(\lambda)$ is 0, i.e. there are no bound states. [Note: You can solve the quartic equation $(\mu+\lambda)^4 = a\lambda$ using Mathematica, and you can see the occurrence of $\sqrt{27a^4 - 256a^3\mu^3}$ at several places. In order to have one or more real solutions, you need $27a - 256\mu^3$ to be positive. This is where you get the above condition.]

When $\lambda = 0$, the energy also vanishes, and we are left with something that looks very much like a zero momentum plane wave. The wave function is distributed uniformly through space.

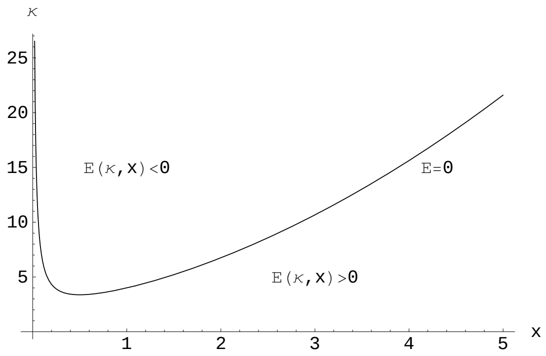

Figure 1: $\kappa = \frac{(1+x)^3}{2x}$

(Of course, this means that the probability of finding the particle at any specific point goes to zero as the volume of space goes to infinity.)

(d) **(5 points)** In terms of our dimensionless variables x and κ, we find (where we have set $\hbar = 1$)

$$\begin{aligned} \mathcal{E} &= \frac{1}{2}\left(\frac{\lambda}{\mu}\right)^2 - \frac{m\alpha}{\mu^2}\left(\frac{\lambda/\mu}{1+\lambda/\mu}\right)^3 \\ &= \frac{1}{2}x^2 - \kappa\left(\frac{x}{1+x}\right)^3. \end{aligned}$$

We would like to know when it is possible to have $\mathcal{E} = 0$, as this is the dividing line between having a bound state and having no bound states. We plot this dividing line as a function of x and κ in figure 1. To have $\mathcal{E} = 0$, we must have $\kappa = \frac{(1+x)^3}{2x}$. The minimum value of κ satisfying that condition is obtained by setting $\frac{\partial \kappa}{\partial x} = 0$, yielding

$$\kappa_{min} = \frac{27}{8} = 3.375, \qquad\qquad x = \frac{1}{2}.$$

(e) **(3 points)** Recall that the variational method gives only an upper bound on the ground state energy. If $\mathcal{E} < 0$, we know that there exists a bound state, but if $\mathcal{E} > 0$, we cannot conclude that there is no bound state. Therefore, the previous section gives us neither a minimum nor a maximum value of α required for a bound state. All it tells us is that if $\alpha \geq \frac{\hbar^2\mu^2\kappa_{min}}{m}$, then we know that a bound state exists, while if $\alpha < \frac{\hbar^2\mu^2\kappa_{min}}{m}$, we do not know if a bound state exists.

4. **Helium atom (15 points)**

(a) **(3 points)** The Hamiltonian is invariant under exchange of 1 and 2, i.e. $[H, P_{12}] = 0$, where P_{12} is the operator which permutes 1 and 2. Thus we can choose the spatial part of energy eigenstates $\Phi(\vec{r}_1, \vec{r}_2)$ to be eigenstates of P_{12}, i.e. symmetric or anti-symmetric under the exchange of 1 and 2.

(b) **(4 points)** The wave function must be anti-symmetric under the exchange of the two electron because of Fermi statistics. ie $\psi(1,2) = -\psi(2,1)$. If Φ is symmetric, the spin part χ can be chosen to be anti-symmetric and vice versa. The spin part is product of two 1/2-spins, which decomposes into two irreducible representations $1/2 \otimes 1/2 = 1 \oplus 0$

If χ is anti-symmetric, then it is in the singlet representation

$$\chi(1,2) = \frac{1}{\sqrt{2}}(|+,-\rangle - |-,+\rangle), \tag{16}$$

and if χ is symmetric, then it is in the vector representation

$$\chi(1,2) = \begin{cases} |+,+\rangle & m = 1, \\ \frac{1}{\sqrt{2}}(|+,-\rangle + |-,+\rangle) & m = 0, \\ |-,-\rangle & m = -1. \end{cases} \tag{17}$$

(c) **(4 points)** If we only have the He^+ ion and a free electron, then the perturbation is zero and the energy is $4E_1$ (where E_1 is the Bohr energy of the ground state of the hydrogen atom. The factor of 4 comes from replacing $e^2 \longrightarrow 2e^2$).

If both of the electrons are in excited states then the eigenvalue for H_0 is $E^{(0)} = 4(E_n + E_{n'}) = 4E_1 \left(\frac{1}{n^2} + \frac{1}{n'^2}\right) > 4E_1$ for n, $n' > 1$. Here $E_1 = -|E_1| = -13.6eV < 0$.

The first order correction in energy is given by $E^{(1)} = \langle\psi_0|H'|\psi_0\rangle$, where ψ_0 is zero-th order wave function. Since H' is positive. $E^{(1)}$ is positive, thus further increasing the energy.

Hence to first order in perturbation theory, the He atom with both the electrons in the excited states has higher energy than that of the He^+ ion and a free electron.

(d) **(4 points)** Since the average radius of electron 2 in the excited state is much larger than that of electron 1 in the ground state, the effective charge felt by 2 is $2e - e = e$.

Given this observation, we can pick

$$V_1(r_1) = -\frac{2e^2}{r_1}, \qquad V_2(r_2) = -\frac{e^2}{r_2} \ . \tag{18}$$