Physics 741 – Graduate Quantum Mechanics 1

Solutions to Chapter 12

1. [25] A particle of mass *m* is contained in the potential $V(x)=\frac{1}{2}\lambda x^4$.

(a) [2] What symmetry does this potential have? What is the likely eigenvalue of the ground state under this symmetry? What is the likely eigenvalue of the first excited state under this symmetry?

Obviously, this potential has parity symmetry, so the eigenstates of the Hamiltonian can also be chosen to be eigenstates of parity. We expect that the ground state will have even parity and the first excited state will have odd parity.

(b) [6] Consider the trial wave function $\psi(x)=\exp\left(-\frac{1}{2}Ax^2\right)$. Does this have the right symmetry properties for the ground state, as given in part (a)? Calculate the normalized expectation value of the Hamiltonian using this wave function.

Since this is an even function, it has the right parity to be an eigenstate of the Hamiltonian, though it is very unlikely that it will be an actual eigenstate. We now calculate

$$\begin{aligned}
\langle\psi|P^2|\psi\rangle &= -\hbar^2\int_{-\infty}^{\infty}\exp\left(-\tfrac{1}{2}Ax^2\right)\frac{\partial^2}{\partial x^2}\exp\left(-\tfrac{1}{2}Ax^2\right)dx=-\hbar^2\int_{-\infty}^{\infty}\left(-A+A^2x^2\right)\exp\left(-Ax^2\right)dx\\
&=\hbar^2\left(AA^{-1/2}\Gamma\left(\tfrac{1}{2}\right)-A^2A^{-3/2}\Gamma\left(\tfrac{3}{2}\right)\right)=\hbar^2\sqrt{A}\left(\sqrt{\pi}-\tfrac{1}{2}\sqrt{\pi}\right)=\tfrac{1}{2}\hbar^2\sqrt{\pi A},\\
\langle\psi|x^4|\psi\rangle &= \int_{-\infty}^{\infty}x^4\exp\left(-Ax^2\right)dx=A^{-5/2}\Gamma\left(\tfrac{5}{2}\right)=\tfrac{3}{4}A^{-5/2}\sqrt{\pi},\\
\langle\psi|\psi\rangle &= \int_{-\infty}^{\infty}\exp\left(-Ax^2\right)dx=A^{-1/2}\Gamma\left(\tfrac{1}{2}\right)=\sqrt{\pi/A}.
\end{aligned}$$

Putting it all together, we have

$$E(A)=\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}=\frac{1}{\langle\psi|\psi\rangle}\left(\frac{1}{2m}\langle P^2\rangle+\frac{1}{2}\lambda\langle x^4\rangle\right)=\sqrt{\frac{A}{\pi}}\left(\frac{\hbar^2\sqrt{\pi A}}{4m}+\frac{\lambda 3\sqrt{\pi}}{2\cdot 4A^2\sqrt{A}}\right)=\frac{\hbar^2A}{4m}+\frac{3\lambda}{8A^2}.$$

(c) [5] Minimize the expectation value and find an estimate of the ground state energy. Can we conclude that the ground state energy is lower than this value?

To minimize this function, we take the derivative and set it equal to zero:

$$0=\frac{dE(A)}{dA}=\frac{\hbar^2}{4m}-\frac{3\lambda}{4A^3}\quad\text{with solution}\quad A=\left(\frac{3\lambda m}{\hbar^2}\right)^{1/3}.$$

Substituting this back into our expression, we have

$$E(A)=\frac{\hbar^2}{4m}\left(\frac{3\lambda m}{\hbar^2}\right)^{1/3}+\frac{3\lambda}{8}\left(\frac{3\lambda m}{\hbar^2}\right)^{-2/3}=\left(\frac{3\lambda\hbar^4}{m^2}\right)^{1/3}\left(\frac{1}{4}+\frac{1}{8}\right)=\frac{3}{8}\left(\frac{3\lambda\hbar^4}{m^2}\right)^{1/3}.$$

This is a good estimate of the ground state energy, and definitely an upper bound on it.

(d) [8] Construct a one-parameter trial wave function with the appropriate symmetry properties for the first excited state. Calculate the normalized expectation value of the Hamiltonian using this wave function.

We want an odd function for the first excited state. An appropriate choice might be $\psi(x) = xe^{-Ax^2/2}$. This can have no mixture of the true ground state in it, since the true ground state is an even function.

As before, we start calculating a variety of messy formulas:

$$\langle\psi|P^2|\psi\rangle = -\hbar^2\int_{-\infty}^{\infty} xe^{-Ax^2/2}\frac{\partial^2}{\partial x^2}\left(xe^{-Ax^2/2}\right)dx = -\hbar^2\int_{-\infty}^{\infty} x\left(-3Ax + A^2x^3\right)e^{-Ax^2}dx$$
$$= \hbar^2\left(AA^{-3/2}3\Gamma\left(\tfrac{3}{2}\right) - A^2A^{-5/2}\Gamma\left(\tfrac{5}{2}\right)\right) = \hbar^2A^{-1/2}\left(\tfrac{3}{2}\sqrt{\pi} - \tfrac{3}{4}\sqrt{\pi}\right) = \tfrac{3}{4}\hbar^2\sqrt{\pi/A},$$
$$\langle\psi|x^4|\psi\rangle = \int_{-\infty}^{\infty} x^6e^{-Ax^2}dx = A^{-7/2}\Gamma\left(\tfrac{7}{2}\right) = \frac{15\sqrt{\pi}}{8A^3\sqrt{A}},$$
$$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} x^2\exp\left(-Ax^2\right)dx = \frac{\Gamma\left(\frac{3}{2}\right)}{A^{3/2}} = \frac{1}{2A}\sqrt{\frac{\pi}{A}}.$$

We put these in to find the energy expectation value, like before.

$$E(A) = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{1}{\langle\psi|\psi\rangle}\left(\frac{1}{2m}\langle P^2\rangle + \frac{1}{2}\lambda\langle x^4\rangle\right) = 2A\sqrt{\frac{A}{\pi}}\left(\frac{3\hbar^2}{8m}\sqrt{\frac{\pi}{A}} + \frac{\lambda 15}{2\cdot 8A^3}\sqrt{\frac{\pi}{A}}\right) = \frac{3\hbar^2A}{4m} + \frac{15\lambda}{8A^2}$$

(e) [4] Minimize the expectation value and find an estimate of the first excited state energy. Can we conclude that the first excited state energy is lower than this value?

We once again set the derivative to zero to find the minimum.

$$0 = \frac{dE(A)}{dA} = \frac{3\hbar^2}{4m} - \frac{15\lambda}{4A^3}, \quad \text{with solution} \quad A = \left(\frac{5\lambda m}{\hbar^2}\right)^{1/3}.$$

We plug this back into the previous equation to get

$$E(A) = \frac{3\hbar^2}{4m}\left(\frac{5\lambda m}{\hbar^2}\right)^{1/3} + \frac{15\lambda}{8}\left(\frac{5\lambda m}{\hbar^2}\right)^{-2/3} = \left(\frac{5\lambda\hbar^4}{m^2}\right)^{1/3}\left(\frac{3}{4} + \frac{3}{8}\right) = \frac{9}{8}\left(\frac{5\lambda\hbar^4}{m^2}\right)^{1/3}.$$

Because the wave function we used was odd, it has a linear combination of the first excited state and other odd functions with higher energy, and the expectation value of the Hamiltonian will be a linear combination of these energies, and therefore bigger than the true energy of the first excited state. Hence this formula is a strict upper bound on the energy.

2. [10] Joe Ignorant is unaware that the hydrogen atom has a known, exact solution, so he attempts to use the variational principle on it. The Hamiltonian is $H = \mathbf{P}^2/2m - ke^2/|\mathbf{R}|$. The trial wave function he decides to try is $\psi(\mathbf{r}) = e^{-Ar^2}$, where A is a variational parameter. Using this trial wave function, estimate the ground state energy. Compare the result with the exact result (7.51) with n = 1.

We proceed exactly as we did before. We need to find

$$\langle\psi|\mathbf{P}^2|\psi\rangle = \left|\mathbf{P}|\psi\rangle\right|^2 = \int d\Omega\int r^2 dr\left|-i\hbar\nabla e^{-Ar^2}\right|^2 = 4\pi\hbar^2\int r^2 dr\left|2\hbar Ar\hat{\mathbf{r}}e^{-Ar^2}\right|^2$$

$$= 16\pi\hbar^2 A^2\int r^4 e^{-2Ar^2}dr = 16\pi\hbar^2 A^2\frac{3\sqrt{2\pi}}{64A^{5/2}} = \frac{3\pi\sqrt{2\pi}\hbar^2}{4\sqrt{A}},$$

$$\langle\psi\left||\mathbf{R}|^{-1}\right|\psi\rangle = \int d\Omega\int r^2 dr\, e^{-Ar^2}r^{-1}e^{-Ar^2} = 4\pi\int re^{-2Ar^2}dr = 4\pi/(4A) = \pi/A,$$

$$\langle\psi|\psi\rangle = \int d\Omega\int r^2 dr\, e^{-Ar^2}e^{-Ar^2} = 4\pi\int r^2 e^{-2Ar^2}dr = 4\pi\frac{\sqrt{2\pi}}{16A^{3/2}} = \frac{\pi\sqrt{2\pi}}{4A^{3/2}}.$$

We completed the integrals with a little help from Maple:

```
> assume(A>0); integrate(r^2*exp(-2*A*r^2),r=0..infinity);
> integrate((r^4*exp(-2*A*r^2),r=0..infinity);
> integrate(r*exp(-2*A*r^2),r=0..infinity);
```

We now proceed to find the energies E (A):

$$E(A) = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{1}{\langle\psi|\psi\rangle}\left(\frac{1}{2m}\langle\mathbf{P}^2\rangle - k_e e^2\left\langle|\mathbf{R}|^{-1}\right\rangle\right) = \frac{4A^{\frac{3}{2}}}{\pi\sqrt{2\pi}}\left(\frac{1}{2m}\frac{3\pi\sqrt{2\pi}\hbar^2}{4\sqrt{A}} - k_e e^2\frac{\pi}{A}\right)$$

$$= \frac{3\hbar^2 A}{2m} - \frac{4k_e e^2\sqrt{A}}{\sqrt{2\pi}}.$$

We take the derivative and set it to zero

$$0 = \frac{d}{dA}E(A) = \frac{3\hbar^2}{2m} - \frac{2k_e e^2}{\sqrt{2\pi A}},$$

$$\sqrt{2\pi A} = \frac{4k_e e^2 m}{3\hbar^2},$$

$$A = \frac{1}{2\pi}\left(\frac{4k_e e^2 m}{3\hbar^2}\right)^2$$

Substituting this back into our expression for $E(A)$, we have

$$E_1 \approx \frac{3\hbar^2}{2m}\frac{1}{2\pi}\left(\frac{4k_e e^2 m}{3\hbar^2}\right)^2 - \frac{4k_e e^2}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\left(\frac{4k_e e^2 m}{3\hbar^2}\right) = \frac{k_e^2 e^4 m}{\hbar^2}\left(\frac{4}{3\pi} - \frac{8}{3\pi}\right) = -\frac{4k_e^2 e^4 m}{3\pi\hbar^2} \approx -0.424\frac{k_e^2 e^4 m}{\hbar^2}.$$

The correct expression is identical, but with a factor of – 0.5 in front instead of – 0.424.