Quantum Mechanics III - Take Home Exam

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1 Question 1

The solution set to the 1-Dimensional infinite potential well on the interval $(0, a)$ is well known and upon projection into position space yields the normalised eigenfunctions and eigenenergies

$$\langle x|\psi_n\rangle = \sqrt{\frac{2}{a}} sin(\frac{n\pi x}{a}) \qquad E_n = \frac{n^2\pi^2\hbar^2}{2Ma^2}$$

Giving the lowest three eigenfunctions and eigenenergies as

$$\langle x|\psi_1\rangle = \sqrt{\frac{2}{a}} sin(\frac{\pi x}{a}) \qquad E_1 = \frac{\pi^2\hbar^2}{2Ma^2}$$

$$\langle x|\psi_2\rangle = \sqrt{\frac{2}{a}} sin(\frac{2\pi x}{a}) \qquad E_2 = \frac{4\pi^2\hbar^2}{2Ma^2}$$

$$\langle x|\psi_3\rangle = \sqrt{\frac{2}{a}} sin(\frac{3\pi x}{a}) \qquad E_3 = \frac{9\pi^2\hbar^2}{2Ma^2}$$

a) First order correction to eigenenergy ϵ_n of eigenstate $|n\rangle$ is given by

$$E_n^{(N)} = \langle n| V |n\rangle$$

For the ground state case $n = 1$ of the infinite square well, using the solutions above, this is

$$\begin{aligned} E_1^{(N)} &= \langle 1| V |1\rangle \\ &= b\int_0^{a/2} dx|\psi_1(x)|^2 + (0)\int_{a/2}^{a} dx|\psi_1(x)|^2 \\ &= b\int_0^{a/2} dx|\psi_1(x)|^2 \end{aligned} \qquad (1)$$

Given that we know the wave function of the ground state solution to the infinite square well to be symmetric about the point $a/2$, we know the probability density will also be symmetric about this point, being 0.5 on both sides. Thus

$$E_1^{(N)} = \frac{b}{2} \tag{2}$$

The second excited state wave function $\psi_2(x)$ is again symmetric about the point $\frac{a}{2}$ and so the same logic holds thus

$$\begin{aligned} E_1^{(N)} &= b\int_0^{a/2} dx|\psi_2(x)|^2 + (0)\int_{a/2}^{a} dx|\psi_2(x)|^2 \\ &= b\int_0^{a/2} dx|\psi_2(x)|^2 \\ &= \frac{b}{2} \end{aligned} \tag{3}$$

b) First order correction to the wave function is

$$\bar{P}_n |N_1\rangle = \sum_{m\neq n} \frac{|m\rangle \langle m| V |n\rangle}{\epsilon^{(n)} - \epsilon^{(m)}}$$

The ground state correction is covered by the case $n = 1$. Note the eigenenergies for the infinite square well given above lead the denominator to take the simplified form

$$\epsilon^{(n)} - \epsilon^{(m)} = \frac{\pi^2\hbar^2}{2Ma^2}\left(n^2 - m^2\right)$$

In the ground state case $n = 1$ this reduces to

$$\frac{\pi^2\hbar^2}{2Ma^2}\left(1 - m^2\right)$$

Evaluating the numerator

$$\langle m| V |1\rangle = b\int_0^{a/2} dx\frac{2}{a}sin\left(\frac{m\pi x}{a}\right) sin\left(\frac{\pi x}{a}\right) + 0$$

Using the relation

$$sin(a)sin(b) = \frac{1}{2}\left(cos(a-b) - cos(a+b)\right)$$

we then have

$$
\begin{aligned}
\langle m| V |1\rangle &= \frac{b}{a}\int_0^{a/2} dx \left(cos\left(\frac{\pi x}{a}(m-1)\right) - cos\left(\frac{\pi x}{a}(m+1)\right)\right) \\
&= \frac{b}{a}\left(\left[\frac{a}{\pi(m-1)} sin\left(\frac{\pi x}{a}(m-1)\right)\right]_0^{a/2} - \left[\frac{a}{\pi(m+1)} sin\left(\frac{\pi x}{a}(m+1)\right)\right]_0^{a/2}\right) \\
&= \frac{b}{\pi}\left[\frac{sin\left(\frac{\pi}{2}(m-1)\right)}{(m-1)} - \frac{sin\left(\frac{\pi}{2}(m+1)\right)}{(m+1)}\right] \\
&= \frac{b}{\pi(m^2-1)}\left[(m-1)sin\left(\frac{\pi}{2}(m-1)\right) - (m+1)sin\left(\frac{\pi}{2}(m+1)\right)\right]
\end{aligned}
\tag{4}
$$

For odd values of m the sine expressions vanishes so we need only consider even values of m. Define a new variable n such that $m = 2n$, the above then becomes

$$
\begin{aligned}
\langle 2n| V |1\rangle &= \frac{b}{\pi(4n^2-1)}\left[(2n-1)(-1)^{n+1} - (2n+1)(-1)^n\right] \\
&= \frac{b}{\pi(4n^2-1)}\left[2n(-1)^{n+1} - (-1)^{n+1} + 2n(-1)^{n+1} + (-1)^{n+1}\right] \\
&= \frac{b}{\pi(4n^2-1)} 4n(-1)^{n+1}
\end{aligned}
\tag{5}
$$

Combining the numerator and denominator the total expression is then

$$
\begin{aligned}
\frac{\langle 2n| V |1\rangle}{\epsilon^1 - \epsilon^{(2n)}} &= \frac{2Ma^2}{\pi^2(1-4n^2)} \frac{4bn(-1)^{n+1}}{\pi(4n^2-1)} \\
&= \frac{4a^2b}{\pi^3(4n^2-1)^2} 2M(-1)^n
\end{aligned}
\tag{6}
$$

And so first order correction to the ground state wave wavefunction is

$$
\sum_{n=1}^{\infty} (-1)^n \frac{8a^2bM}{\pi^3(4n^2-1)^2} |2n\rangle
$$

c) Take the second order correction to the energy

$$
E = \sum_{m \neq n} \frac{\langle n| H |m\rangle \langle m| H |n\rangle}{\epsilon^{(n)} - \epsilon^{(m)}}
$$

In the closure approximation[1] we assume the denominator to be approximated by some average energy separation

$$\Delta E \approx \epsilon^{(m)} - \epsilon^{(n)}$$

So approximation for the second order correction is then given by

$$E' = \frac{-1}{\Delta E} \sum_{m \neq n} \langle n| H |m\rangle \langle m| H |n\rangle$$

Altering the sum to include the case $m = n$ by subtracting outside the sum, then invoking the completeness relation gives

$$E' = \frac{-1}{\Delta E} \langle n| H^2 |n\rangle + \frac{1}{\Delta E} \left(\langle n| H |n\rangle\right)^2$$

Solving the first term for the ground state case $n = 1$

$$\begin{aligned} \langle 1| H^2 |1\rangle &= \langle 1| (H_0 + V)(H_0 + V) |1\rangle \\ &= \langle 1| H_0^2 + 2VH_0 + V^2 |1\rangle \end{aligned} \tag{7}$$

Each term evaluated independently gives

$$\langle 1| H_0^2 |1\rangle = \epsilon_1^2$$

$$\langle 1| 2VH_0 |1\rangle = 2b \int_0^{a/2} dx \psi_1(x) H_0 \psi_1(x)$$

$$\begin{aligned} H_0\psi_1(x) &= \frac{-1}{2M} \frac{d^2}{dx^2} \sqrt{\frac{2}{a}} sin(\frac{\pi x}{a}) \\ &= \frac{\pi^2}{2Ma^2} \psi_1(x) \end{aligned} \tag{8}$$

So

$$\langle 1| 2VH_0 |1\rangle = \frac{b\pi^2}{Ma^2} \int_0^{a/2} dx |\psi_1(x)|^2$$

Since the ground state wave function is symmetric about $a/2$ so is its probability density and hence the integral evaluates to 0.5 giving

$$\langle 1| 2VH_0 |1\rangle = \frac{b\pi^2}{2Ma^2}$$

In part (a) we found

$$\langle 1| V |1\rangle = \frac{b}{2}$$

And from the same logic

$$\langle 1| V^2 |1\rangle = \frac{b^2}{2}$$

Combining all the above gives

$$\langle 1| H^2 |1\rangle = \epsilon_1^2 + \frac{b\pi^2}{2Ma^2} + \frac{b^2}{2}$$

Second expression is given by

$$\begin{aligned} \langle 1| H |1\rangle &= \langle 1| H_0 |1\rangle + \langle 1| V |1\rangle \\ &= \epsilon_1 + \frac{b}{2} \end{aligned} \tag{9}$$

So

$$(\langle 1| H |1\rangle)^2 = \epsilon_1^2 + b\epsilon_1 + \frac{b^2}{4}$$

So total approximation for the correction to the energy is

$$\begin{aligned} E' &= \frac{1}{\Delta E}\left(\epsilon_1^2 + b\epsilon_1 + \frac{b^2}{4} - \epsilon_1^2 - \frac{b\pi^2}{2Ma^2} - \frac{b^2}{2}\right) \\ &= \frac{1}{\Delta E}\frac{-b^2}{4} \end{aligned} \tag{10}$$

Where ΔE can be chosen as to be a reasonable average of the energy spacings. Setting this as the maximum it can be

$$\begin{aligned} \Delta E &= \epsilon^2 - \epsilon^1 \\ &= \Delta E = \frac{\pi^2}{2Ma^2}(4-1) \\ &= \frac{3\pi^2}{2Ma^2} \end{aligned} \tag{11}$$

And so approximate energy upper bound is then

$$\frac{8Ma^2}{3\pi^2}\frac{-b^2}{4} = \frac{2Ma^2}{3\pi^2}$$

2 Question 2

Upper bound to the ground state energy E_0 is given by

$$E_0 \leq \frac{\langle\psi| H |\psi\rangle}{\langle\psi|\psi\rangle}$$

Where H is the hamiltonian in question. Note the trial function $Ae^{\frac{-r}{a}}$ is in terms of r, thus it is reasonable to expand the laplacian of

$$H = \frac{-1}{2m}\nabla^2 + k\frac{r^2}{2}$$

in spherical coordinates. Evaluating each part of the upper bound separately gives

$$\begin{aligned}\langle\psi|\psi\rangle &= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta sin(\theta) \int_0^{\infty} drr^2 A^2 e^{\frac{-2r}{a}} \\ &= 4\pi A^2 \int_0^{\infty} drr^2 e^{\frac{-2r}{a}}\end{aligned} \tag{12}$$

Making use of the relation

$$\int_0^{\infty} dx x^n e^{-bx} = \frac{n!}{a^{n+1}}$$

We have

$$\begin{aligned}\langle\psi|\psi\rangle &= 4\pi A^2 \left(\frac{2!}{(\frac{2}{a})^3}\right) \\ &= 4\pi A^2 \left(\frac{2a^3}{8}\right) \\ &= \pi A^2 a^3\end{aligned} \tag{13}$$

The hamiltonian term is given by

$$\langle\psi| H |\psi\rangle = \frac{-1}{2m} \langle\psi| \nabla^2 |\psi\rangle + \frac{k}{2} \langle\psi| r^2 |\psi\rangle$$

Since

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) = \frac{2}{r}\frac{d}{dr} + \frac{d^2}{dr^2}$$

So

$$\nabla^2 A e^{\frac{-r}{a}} = \frac{-2}{ar} A e^{\frac{-r}{a}} + \frac{1}{a^2} A e^{\frac{-r}{a}}$$

So

$$\begin{aligned}
\langle\psi| \nabla^2 |\psi\rangle &= 4\pi \int_0^\infty dr r^2 \left(\frac{-2}{ar} A^2 e^{\frac{-2r}{a}} + \frac{1}{a^2} A^2 e^{\frac{-2r}{a}} \right) \\
&= 4\pi A^2 \left(\frac{-2}{a} \int_0^\infty dr r e^{\frac{-2r}{a}} + \frac{1}{a^2} \int_0^\infty dr r^2 e^{\frac{-2r}{a}} \right) \\
&= 4\pi A^2 \left(\frac{-2}{a} \frac{a^2}{4} + \frac{1}{a^2} \frac{a^3}{4} \right) \\
&= -\pi A^2 a
\end{aligned} \tag{14}$$

The second term is given by

$$\begin{aligned}
\langle\psi| r^2 |\psi\rangle &= 4\pi \int_0^\infty dr r^4 A^2 e^{\frac{-2r}{a}} \\
&= 4\pi A^2 \left(\frac{4!}{\left(\frac{2}{a}\right)^5} \right) \\
&= 4\pi A^2 \frac{24a^5}{32} \\
&= 3\pi A^2 a^5
\end{aligned} \tag{15}$$

And so total expression is

$$\begin{aligned}
\langle\psi| H |\psi\rangle &= \frac{-1}{2m} \langle\psi| \nabla^2 |\psi\rangle + \frac{k}{2} \langle\psi| r^2 |\psi\rangle \\
&= \frac{-1}{2m} (-\pi a) + \frac{k}{2} \pi A^2 3\pi a^5 \\
&= \frac{\pi a}{2m} + \frac{3\pi a^5 k}{2}
\end{aligned} \tag{16}$$

Now combining numerator and denominator to find upper bound for E_0 we have

$$\frac{\langle\psi| H |\psi\rangle}{\langle\psi|\psi\rangle} = \frac{1}{2ma^2} + \frac{3a^2 k}{2} \tag{17}$$

Finding the minimum of this upper bound by taking the derivative with respect to a and setting it equal to zero

$$\frac{d}{da}\left(\frac{1}{2ma^2} + \frac{3a^2 k}{2} \right) = \frac{-1}{ma^3} + 3ak = 0$$

$$3ak = \frac{1}{ma^3}$$
$$a^4 = \frac{1}{3mk}$$
$$a^2 = \sqrt{\frac{1}{3mk}}$$

Substituting this minimum for a into our expression for the energy upper bound

$$\begin{aligned} E_0 &\leq \frac{1}{2ma^2} + \frac{3a^2k}{2} \\ &= \sqrt{\frac{3mk}{4m^2}} + \sqrt{\frac{9k^2}{12mk}} \\ &= \frac{\sqrt{3}}{2}\sqrt{\frac{k}{m}} + \frac{\sqrt{3}}{2}\sqrt{\frac{k}{m}} \end{aligned} \tag{18}$$

Recalling the oscillation frequency is defined as $\omega = \sqrt{\frac{k}{m}}$ we then have

$$E_0 \leq \sqrt{3}\omega$$

as an upper bound for the ground state energy. This gives a value of approximately 1.7321ω, noting the exact solution is 0.5ω. So our upper bound is out by approximately 1.2321ω.

3 References

(1) *https : //www.southampton.ac.uk/assets/centresresearch/documents/compchem /perturbation_theory.pdf*