1. Making Waves, Down on the $\delta$

In class, we discussed the case of a 1-D infinite square well, extending over the range $0 < x < a$, but with half of the well at a potential energy of $V_0$. To first order, this raised the energy of each state by $V_0/2$, which seemed reasonable.

Suppose instead that we perturb the well by placing a delta function in the middle, so that

$$H' = \kappa \delta(x - a/2)$$

where $\kappa$ is a positive constant, and equal to the area under the ‘spike.’

(a) For this potential, calculate the first-order energy correction, or shift, for each level of the well.

(b) Explain in words why this correction vanishes for all even $n$, but not for the odd $n$ states. If you’re stuck, think about the shape of the associated wave functions.

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**SOLUTION**

(a) For the unperturbed (no $H'$) 1-D infinite square well described above, recall that the normalized wave function for the $n^{th}$ state is given by

$$\psi^0_n(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi x}{a} \right)$$

Thus, using the expression derived in class, we can now calculate the first-order correction to the energy levels of the well for the perturbing delta function. We have

$$E^1_n = \langle \psi^0_n | H' | \psi^0_n \rangle$$

$$= \frac{2}{a} \kappa \int_0^a \sin^2 \left( \frac{n\pi x}{a} \right) \delta(x - a/2) \, dx$$

To do the above integral, we first remind ourselves of how a Dirac $\delta$-function “works.” Roughly speaking, the function $\delta(x - x_0)$ is a tall ‘spike’ at the point $x_0$, i.e., it is zero for all $x \neq x_0$, and goes to infinity at $x = x_0$. More formally, one could argue that the Dirac $\delta$-function really only makes sense when integrated over, as the spike has no width.
and infinite height, but is defined to be of unit area ‘under the curve.’ (Sorry for all the quotes, but $\delta(x)$ is hardly even a function, in any real sense!) Thus, we can define the Dirac $\delta$-function operationally as

$$\int_{x_a}^{x_b} \kappa \delta(x - x_0) \, dx = \begin{cases} \kappa & \text{if } x_a < x_0 < x_b \\ 0 & \text{otherwise} \end{cases}$$

Much more importantly, this means that if our integrand contains a delta function whose argument equals zero within our limits of integration, then doing the integral reduces to simply evaluating the integrand at that point, so

$$\int_{x_a}^{x_b} \kappa \delta(x - x_0) f(x) \, dx = \kappa f(x_0)$$

Armed with the above, we can now finish the problem. We see

$$E_n^1 = \frac{2}{a} \kappa \int_0^a \sin^2 \left( \frac{n\pi x}{a} \right) \delta(x - a/2) \, dx$$

$$= \frac{2\kappa}{a} \sin^2 \left( \frac{n\pi}{2} \right)$$

Evaluating the sine function for integer $n$, we obtain our final answer that

$$E_n^1 = \begin{cases} 0 & \text{if } n \text{ is even} \\ 2\kappa/a & \text{if } n \text{ is odd} \end{cases}$$

(b) With a bit of thought, we can see why there should be no effect on the even-$n$ states. For these states, their wave functions are such that an even number of half-waves exactly fit inside the well, and so they will all have a node (zero-crossing) in the middle of the well. The probability density $|\psi_n^0(x)|^2$ – the function indicating where the particle is most likely to be found – therefore equals zero at the point $x = a/2$. This means there is no probability of the particle being there if it is in a state of even $n$. Thus, the particle will never ‘feel’ the perturbation, and its energy can not be affected by it.

For the odd states, on the other hand, the probability density has an anti-node right at the perturbing potential, and so any particle in such a state will experience a positive shift in its energy.
2. Well, well, well...

When we consider a 1-D infinite square well, the potential $V(x)$ is taken to go to $+\infty$ at all $x$ values except for some range $0 < x < a$, over which $V = 0$. For this problem, $V$ still goes to infinity everywhere outside $0 < x < a$, but within this range, $V(x)$ does not vanish, but rather has the shape

$$V(x) = \varepsilon \sin \left(\frac{\pi x}{a}\right) \quad 0 < x < a$$

Taking $\varepsilon$ to be a small positive quantity, calculate the shift in energy of all the bound states to first order, that is, determine $E_n^{(1)}$ for all $n$. Given the shape of the perturbing potential, does its effect on the ground state energy seem reasonable? Why or why not?

**SOLUTION**

In this problem, we are basically dealing with an infinite square well, except the bottom of the well bows slightly upward. This means that the particle’s potential energy will be slightly more, and its kinetic energy slightly less, near $a/2$ than at $x = 0$ or $a$. The result is that our (unperturbed) sine wave solutions will be ‘stretched’ near the middle, which in turn will effect the energies $E_n$ at which a particular solution ‘fits’ inside the well. It should also be clear that in the limit of $\varepsilon \to 0$ we indeed regain our usual well, for which we know the eigensolutions analytically. Thus, in our new terminology

$$H' = \varepsilon \sin \left(\frac{\pi x}{a}\right) \quad \text{for } 0 < x < a$$

and

$$\psi_n^{(0)} = \sqrt{\frac{2}{a}} \sin \left(\frac{n\pi x}{a}\right)$$

with

$$E_n^{(0)} = \frac{\hbar^2 \pi^2}{2ma^2} n^2$$

Because these energies are non-degenerate (for the 1-D case), we can immediately write down the first-order energy correction. We have

$$E_n^{(1)} = H_{nn} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = \varepsilon \int_{-\infty}^{+\infty} |\psi_n^{(0)}|^2 \sin \left(\frac{\pi x}{a}\right) dx$$

Once we substitute in the correct form for our unperturbed wave function, we see that the problem is reduced to that of evaluating the integral

$$E_n^{(1)} = \varepsilon \frac{2}{a} \int_0^a \sin^2 \left(\frac{n\pi x}{a}\right) \sin \left(\frac{\pi x}{a}\right) dx$$

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As usual, I find it helpful to switch to the dimensionless variable \( z = (\pi/a)x \), so \( x = (a/\pi)z \). This leaves us with the (somewhat) more intuitive integral

\[
E_n^{(1)} = \varepsilon \frac{2}{\pi} \int_0^\pi \sin^2(nz) \sin(z) \, dz
\]

We immediately recognize this as a definite integral that lends itself perfectly to the “look it up in a book” technique (my personal favorite), or the “I hope Mathematica / Maple / my calculator can handle this” approach. One way or another, you should obtain

\[
I_n \equiv \int_0^\pi \sin^2(nz) \sin(z) \, dz = \frac{4n^2}{4n^2 - 1}
\]

Rather than just adding a few constants out front and declaring victory, this is a good time to ask if the above seems plausible. Note that the result can depend only on the parameter \( n \), so we are really asking about its \( n \)-dependence. After staring at the above expression for a few minutes, we see there are two limiting cases which are easy to analyze:

1) \( n = 1 \)

In this case, we can do the original integral easily. We have

\[
I_1 = \int_0^\pi \sin^3(z) \, dz = \left[ \frac{\cos^3 z}{3} - \cos z \right]_0^\pi = -\frac{1}{3} - \frac{1}{3} - (-1) + 1 = \frac{4}{3}
\]

which agrees with our expression above for \( n = 1 \). This is also the case where the effect is largest, which seems reasonable because the wave is ‘in sync’ with the perturbation.

2) \( n \to \infty \)

To evaluate the integral in this limit, we note that \( \sin^2(nz) \) becomes a rapidly oscillating function whose average value over any range is just 1/2. Thus, in this limit we have

\[
I_\infty = \frac{1}{2} \int_0^\pi \sin(z) \, dz = \frac{1}{2} \cdot 2 = 1
\]

which also agrees with our general result. So the above expression for \( I_n \) seems reasonable, and we probably haven’t lost a factor of 2 or \( \pi \) somewhere.

Finally, we use this expression to obtain the desired result

\[
E_n^{(1)} = \varepsilon \frac{2}{\pi} I_n = \frac{8 \varepsilon n^2}{\pi (4n^2 - 1)}
\]

Because \( \varepsilon \) is positive, the “floor” of the potential well bows upward, so we might expect that all energy levels would be raised to higher values. And indeed, the energy shift is seen to be positive in this case, and in general will just track the sign of \( \varepsilon \).
3. The Anisotropic SHO Must Go On! (15 pts)

Consider the interesting problem of a charged particle (charge = e) in a 1-D SHO potential that is immersed in a uniform electric field. In this case, we pick up an extra potential term of the form $\mathcal{H}' = e\mathcal{E}x$, where $\mathcal{E}$ is the electric field strength. For this problem, calculate the shift in the energy level of the $n^{th}$ state to second order in the “small” quantity $(e\mathcal{E})$. Along the way, show that the first-order correction vanishes for all $n$. Hint: consider using raising and lowering operators, rather than working in a coordinate representation.

**SOLUTION**

Working in 1-D, this is a straightforward application of non-degenerate perturbation techniques, so let’s just jump right in. We showed in lecture that the general form for the first-order energy shift of the state $\psi_n$ due to a perturbation $\mathcal{H}'$ is given by

$$E_{n}^{(1)} = H'_{nn} \equiv \langle \psi_n^{(0)} | \mathcal{H}' | \psi_n^{(0)} \rangle$$

For this particular problem, this takes the form

$$E_{n}^{(1)} = e\mathcal{E} \langle n|x|n \rangle$$

where for brevity we denote the unperturbed eigenfunctions simply by their (only) quantum number $n$, that is, $|n\rangle \equiv |\psi_n^{(0)}\rangle$.

There are several ways to evaluate this matrix element. We could use coordinate space representations of the wave functions, $\psi_n^{(0)}(x)$, and integrate over all space. Alternatively, and more elegantly, we could re-write the operator $x$ in terms of the raising and lowering operators $a_+$ and $a_-$. Either way, it is easy to see that the matrix element (and hence the first-order energy shift) must be zero. If we work in coordinate space, for example, we know that each wave function is either even or odd in $x$, and so its square, $|\psi_n^{(0)}(x)|^2$, must be even in $x$, for all $n$. The operator $x$, of course, is odd. Thus, the full integrand will be odd in $x$, and will therefore vanish when integrated from $-\infty$ to $+\infty$.

Using raising and lowering operators, we recall from last semester (maybe) or from looking back in Chapter 2 (more likely) that we can write

$$x = \left( \frac{\hbar}{2m\omega} \right)^{1/2} (a_+ + a_-)$$

When applied to a state $|n\rangle$, we see that the operator $x$ will cause $n$ to both increase and decrease by 1, resulting in a linear combination of two states ($|n+1\rangle$ and $|n-1\rangle$) that are each orthogonal to $|n\rangle$. So again, we find $\langle n|x|n \rangle = 0$. 

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We now follow the same procedure to determine the second-order energy shift. Recalling that the allowed energies for a 1-D SHO are given by $E_{n}^{0} = n\hbar \omega + \frac{1}{2}$, we find that

$$E_{n}^{(2)} = \sum_{m \neq n} \frac{|H_{mn}|^2}{E_{n}^{0} - E_{m}^{0}} = \left(e\mathcal{E}\right)^2 \sum_{m \neq n} \frac{|\langle m|x|n\rangle|^2}{\hbar \omega (n - m)}$$

To evaluate the matrix element $\langle m|x|n\rangle$, I will use the operator approach. Inserting the expression for $x$ given on the previous page, we find

$$E_{n}^{(2)} = \left(e\mathcal{E}\right)^2 \left(\frac{\hbar}{2m\omega}\right) \sum_{m \neq n} \frac{|\langle m|a_{+} + a_{-}|n\rangle|^2}{\hbar \omega (n - m)} = \frac{e^2\mathcal{E}^2}{2m\omega^2} \sum_{m \neq n} \frac{|\langle m|a_{+} + a_{-}|n\rangle|^2}{n - m}$$

Turning to the matrix element itself, we look back in Ch. 2 and find

$$(a_{+} + a_{-})|n\rangle = (n + 1)^{1/2}|n + 1\rangle + n^{1/2}|n - 1\rangle$$

Thus, in our sum over $m$, all terms will clearly vanish except for the $a_{+}$ piece when $m = n + 1$ and the $a_{-}$ piece when $m = n - 1$. Using this, we see

$$\sum_{m \neq n} \frac{|\langle m|a_{+} + a_{-}|n\rangle|^2}{n - m} = \frac{|\sqrt{n + 1}|^2}{n - (n + 1)} + \frac{|\sqrt{n}|^2}{n - (n - 1)} = \frac{n + 1}{-1} + \frac{n}{1} = -1$$

Putting this all together, we therefore find that, to second order,

$$E_{n} = E_{n}^{(0)} + E_{n}^{(2)} = \hbar \omega \left(n + \frac{1}{2}\right) - \frac{e^2\mathcal{E}^2}{2m\omega^2}$$

This is our final result. Perhaps surprisingly, we see that the energy shift due to the electric field is independent of $n$. To help our intuition, we can rewrite the potential energy as

$$V_{tot} = \frac{1}{2}m\omega^2x^2 + e\mathcal{E}x$$

$$= \frac{1}{2}m\omega^2 \left( x^2 + 2\frac{e\mathcal{E}}{m\omega^2}x \right)$$

$$= \frac{1}{2}m\omega^2 \left( x + \frac{e\mathcal{E}}{m\omega^2} \right)^2 - \frac{e^2\mathcal{E}^2}{2m\omega^2}$$

Though this last expression seems much more complicated than the original, it has a really nice interpretation: the effect of the electric field is to shift the center of the potential (the equilibrium point) by $-e\mathcal{E}/m\omega^2$, and lower the energy by a constant $e^2\mathcal{E}^2/2m\omega^2$. The lowering of the energy is exactly what we see in our expression for $E_{n}$; and the mysterious ‘shift’ is just the analog of what happens classically for a mass hanging vertically on a spring in the presence of a uniform gravitational field (with $e\mathcal{E} \rightarrow mg$) – it just stretches the spring by a fixed amount, to a new equilibrium position.
4. Rutherford was Right! The Nucleus is Not a Point (15 pts)

In this problem, we revisit the simple hydrogen atom, but we allow the nucleus to have a finite size. Specifically, we want to examine the case of a single electron bound in the electric field of a nucleus of charge $Ze$ and radius $r_0$. If this charge is uniformly distributed over the spherical nucleus, then it is easy to show using Gauss’ Law that the electron ‘sees’ an electrostatic potential

$$V(r) = \begin{cases} 
  k\frac{Ze^2}{2r_0} \left( \frac{r^2}{r_0^2} - 3 \right) & r \leq r_0 \\
  -k\frac{Ze^2}{r} & r > r_0
\end{cases}$$

(a) Defining the perturbation to be the \textit{difference} between $V(r)$ above and a point Coulomb potential, show that the first-order energy shift is given by

$$\Delta E_{n\ell} = k\frac{Ze^2}{2r_0} \int_0^{r_0} \left[ R_{n\ell}(r) \right]^2 \left( \frac{r^2}{r_0^2} + \frac{2r_0}{r} - 3 \right) r^2 \, dr$$

(b) With the approximation $R_{n\ell}(r) \approx R_{n\ell}(0)$ inside the nucleus, show that your expression from part a reduces to

$$\Delta E_{n\ell} = ke^2 \frac{2}{5} \frac{r_0^3}{n^3 a_0^3} \frac{Z^4}{\delta b_0}$$

Explain why the assumption made above for $R_{n\ell}(r)$ is very reasonable, and thus why the Kronecker $\delta$-function that appears in the answer is just what you would expect.

**SOLUTION**

This problem isn’t too bad, once we understand the idea behind it. In our discussions of the hydrogen atom so far, we treated the proton (or nucleus) as a simple point, \textit{i.e.}, a charge $Ze$ concentrated at the origin. This isn’t too bad an approximation, given that the size of a typical nucleus is 4-5 orders of magnitude smaller than a typical Bohr radius. Nevertheless, we can estimate the error in this assumption by modeling the nucleus as a sphere of radius $r_0$, with its charge $Ze$ distributed uniformly over its volume. Using Gauss’ Law shows that this leads to a potential energy with the radial dependence

$$V_{\text{sph}}(r) = \begin{cases} 
  kZe^2 \left( \frac{r^2}{2r_0^3} - \frac{3}{2r_0} \right) & r \leq r_0 \\
  -kZe^2 \frac{1}{r} & r > r_0
\end{cases}$$

where I’ve added the subscript ‘sph’ to remind us that this is the classical electric potential for a uniform sphere of charge.
Outside the nucleus \((r > r_0)\), the potential is just what one expects for a point charge, defined so that \(V(r) \to 0\) as \(r \to \infty\). Inside the nucleus, the potential grows as \(r^2\) (make sure you understand why!), and the constant in the expression has been chosen to ensure that \(V_{\text{sph}}(r)\) has the correct value at the nuclear surface, \(r = r_0\), so that the potential is continuous at all \(r\).

The above is what we will call the “sph” radial dependence, while the simpler \(1/r\) potential we can call the “point” version. We can then write down the full Hamiltonian as:

\[
H = T + V_{\text{sph}} = T + V_{\text{point}} + (V_{\text{sph}} - V_{\text{point}}) \equiv H^0 + H'
\]

Expressed in this form, we can identify the first two terms as \(H^0 = T + V_{\text{point}}\), the problem we have solved in class, and the difference of our two radial potentials, \(V_{\text{sph}} - V_{\text{point}}\), so our perturbation \(H'\). Note that \(H'\) is zero for all \(r > r_0\), or everywhere outside the nucleus.

\((a)\) With the above ideas in mind, we can now use perturbation theory to estimate the shift in the atomic energy levels due to the finite size of a nucleus. It is important to note that our perturbation \(H'\) depends only on the radial coordinate \(r\), and so it can not ‘connect’ states of different angular shape, as discussed in class. What this means in practice is that \(H'\) will be diagonal in the basis of our usual set of states (the \(\{\psi_{n\ell m}\}\) we obtained back in Ch. 4), and so we can safely ignore the fact that, in general, the energy levels of hydrogen are degenerate. This simplifies our work enormously! By choosing to work with this set of states, we are able to use the techniques of non-degenerate perturbation theory, and can proceed to calculate the expectation value of the operator \(H'\) for the state of interest. Thus, we must evaluate

\[
E_{n\ell}^{(1)} = \langle \psi_{n\ell m}^{(0)} | (V_{\text{sph}} - V_{\text{point}}) | \psi_{n\ell m}^{(0)} \rangle
\]

We now have to turn this into an actual integral over all space. Our first step is to note (again) that because \(H'\) is purely radial, i.e., has no angular dependence, performing the integrations over \(\theta\) and \(\phi\) will give us unity. This is just our usual normalization condition on the spherical harmonics. We are then left with just the radial integral

\[
E_{n\ell}^{(1)} = \int_0^\infty |R_{n\ell}(r)|^2 (V_{\text{sph}} - V_{\text{point}}) r^2 dr = kZe^2 \int_0^{r_0} |R_{n\ell}(r)|^2 \left( \frac{r^2}{2r_0^3} - \frac{3}{2r_0} + \frac{1}{r} \right) r^2 dr = kZ^2 e^2 \int_0^{r_0} |R_{n\ell}(r)|^2 \left( \frac{r^2}{r_0^3} + \frac{2r_0}{r} - 3 \right) r^2 dr
\]

which we wanted to show. It is important to note that the limits of integration change because \(H' = 0\) (since \(V_{\text{sph}} = V_{\text{point}}\)) for all \(r > r_0\), as mentioned above.
(b) To do this integral exactly is extremely messy – but because the nuclear radius $r_0$ is so small (a few $\times 10^{-15}$ m) compared to the typical scale over which $R_{n\ell}(r)$ varies ($\sim a_{\text{Bohr}} = a_0 \approx 10^{-10}$ m), we can just approximate the radial wave function by its value at the origin, and assume that $R_{n\ell}(r) = R_{n\ell}(0)$ is reasonable over the whole range of integration. However, we also know that the radial wave function $R_{n\ell}(r)$ vanishes at the origin for all $\ell \neq 0$ (see Eq. 4.75 in the text, for example), so we need to only consider radial waves with $\ell = 0$. Thus, our problem reduces to that of determining the value of the radial waves at the origin for states with $\ell = 0$, that is, finding the value of $R_{n0}(r=0)$. We can do this from the equations on page 152, by working out what the associated Laguerre polynomials do at the origin, or we can ‘cheat’ and use Table 4.7 on page 154. Reading off the values of $R_{n0}(0)$ for $n = 1, 2, 3, 4$, we can reason inductively and guess (correctly) that

$$|R_{n0}(0)|^2 = 4 \left(\frac{Z}{na_0}\right)^3$$

With this simplification, we can now calculate the energy shift as

$$E_{n\ell}^{(1)} = \frac{kZ^2}{2r_0} \cdot 4 \left(\frac{Z}{na_0}\right)^3 \delta_{\ell 0} \int_0^{r_0} \left(\frac{r^4}{r_0^2} + 2r_0r - 3r^2\right) dr$$

$$= \frac{2kZ^4e^2}{n^3a_0^3r_0} \delta_{\ell 0} \left[r_0^5 \frac{r^5}{5r_0^2} + r_0r^2 - r^3\right]_0^{r_0}$$

$$= \frac{2kZ^4e^2}{n^3a_0^3r_0} \delta_{\ell 0} \left[\frac{r_0^3}{5} + r_0^3 - r_0^3\right]$$

$$= \frac{2kZ^4e^2r_0^2}{5n^3a_0^3} \delta_{\ell 0} = \frac{2}{5} r_0^2 \frac{Z^4}{n^3a_0^3} \delta_{\ell 0}$$

or, grouping terms more naturally,

$$E_{n\ell}^{(1)} = \frac{2}{5} r_0^2 (kZe^2) \left(\frac{Z}{na_0}\right)^3 \delta_{\ell 0}$$

This is indeed a small effect. To see how small, we can compare the energy shift to the magnitude of the energy level itself. With a little algebra, we find that

$$\frac{E_{n\ell}^{(1)}}{E_{n\ell}^{(0)}} = \frac{4}{5} Z^2 n^2 \left(\frac{r_0}{a_0}\right)^2 \delta_{\ell 0}$$

The scale is set, as expected, by the ratio of the nuclear radius to that of the electron orbit (Bohr) radius, $r_0/a_0$, which appears quadratically. The smallness of this ratio, about $10^{-5}$, means for a small nucleus like a proton ($Z = 1$), the low $n$ states will be shifted in energy by about a part in $10^{10}$. The smallness of this ratio also justifies the approximation that the radial wave function hardly changes over the size of the nucleus. Finally, the centrifugal pseudoforce that arises if the electron has any net angular momentum drives the radial wave function to zero at the origin, and so the effect vanishes unless $\ell = 0$. 

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