1. In Case of Charged Oscillators, Use the Ladders

A charged particle $e$ is trapped in a 1-D SHO potential that is immersed in a uniform electric field $\mathcal{E}$. In this case, we pick up an extra potential energy term of the form $\mathcal{H}' = e\mathcal{E}x$. Based on this, 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: use raising and lowering operators, rather than working in coordinate space.*

**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 $\hat{H}'$ is given by

$$E_n^{(1)} = H'_{nn} \equiv \langle \psi^{(0)}_n | \hat{H}' | \psi^{(0)}_n \rangle$$

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, $|n\rangle \equiv |\psi^{(0)}_n\rangle$.

There are several ways to evaluate this matrix element. We *could* use coordinate space representations of the wave functions, $\psi^{(0)}_n(x)$, 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, $|\psi^{(0)}_n(x)|^2$, 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 $\langle n|x|n\rangle = 0$.

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 $E_n = \hbar\omega n + \frac{1}{2}$, we find that

$$E_n^{(2)} = \sum_{m \neq n} \frac{|H_{mn}|^2}{E_n^0 - E_m^0} = (\epsilon E)^2 \sum_{m \neq n} \frac{|\langle m|x|n\rangle|^2}{\hbar\omega(n-m)}$$

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

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

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

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

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

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

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 a bit, we rewrite the potential energy in the form

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

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

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

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 $-\epsilon E/m\omega^2$, and lower the energy by a constant $\epsilon^2 \mathcal{E}^2/2m\omega^2$. 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 $\epsilon E \to mg$) – it just stretches a bit, to a new equilibrium position.
2. Rutherford was Right! The Nucleus is Not a Point

Consider a single electron in the electric field of a nucleus of charge $Ze$ and radius $r_0$. If the charge is uniformly distributed over the spherical nucleus, then Gauss’ Law tells us that classically the electron has an electrostatic potential energy of (with $k \equiv 1/4\pi\varepsilon_0$):

$$V(r) = k\frac{Ze^2}{2r_0} \left( \frac{r^2}{r_0^2} - 3 \right) \quad r \leq r_0$$

$$= -k\frac{Ze^2}{r} \quad r > r_0$$

(a) Defining the perturbation to be the difference between $V(r)$ above and the potential energy due to a point charge, 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

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

Explain why the assumption made for $R_{n\ell}(r)$ is reasonable, and why the $\delta$-function in the answer is just what you might expect.

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SOLUTION

In our discussion of the hydrogen atom, we treated the proton (or nucleus) as a point, i.e., a charge $Ze$ concentrated at the origin. This isn’t a bad 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

$$V(r) = kZe^2 \left( \frac{r^2}{2r_0^2} - \frac{3}{2r_0} \right) \quad \text{for } r \leq r_0$$

$$= -kZe^2 \frac{1}{r} \quad \text{for } r > r_0$$

where the constant in the first expression ensures that $V(r)$ has the correct value at the nuclear surface, $r = r_0$. We will call the above the “true” radial dependence, while the $1/r$ potential is the “Coul” version. We can then write down the “true” Hamiltonian:

$$H = T + V_{\text{true}} = T + V_{\text{Coul}} + (V_{\text{true}} - V_{\text{Coul}}) \equiv H^0 + H'$$

Expressed in this form, we can identify $H^0 = T + V_{\text{Coul}}$ as the problem we have solved in class, and the difference of our two radial potentials as our perturbation.
(a) We can now use standard techniques to estimate the shift in the energy levels due to the finite size of a nucleus. We first note that our perturbation $H'$ depends only on the radial coordinate $r$, so it can not ‘connect’ states of different angular shape. What this means in practice is that $H'$ will be diagonal in the states $\{ \psi_{n\ell m} \}$ for a given $n$; so although the energy levels of hydrogen are degenerate, we can use non-degenerate methods and evaluate

$$E_{n\ell}^{(1)} = \langle \psi_{n\ell m}^{(0)} | V_t - V_C | \psi_{n\ell m}^{(0)} \rangle$$

We now have to turn this into an actual integral over all space. Our first step is to note that because $H'$ is purely radial, i.e., has no angular dependence, performing the integrations over $\theta$ and $\phi$ will just give us unity. Our radial integral is then

$$E_{n\ell}^{(1)} = \int_0^\infty |R_{n\ell}(r)|^2 (V_t - V_C) r^2 dr$$

$$= kZe^2 \int_0^{r_0} |R_{n\ell}(r)|^2 \left( \frac{r^2}{2r_0^3} - \frac{3}{2r_0} + \frac{1}{r} \right) r^2 dr$$

$$= kZe^2 \frac{4}{2r_0} \int_0^{r_0} |R_{n\ell}(r)|^2 \left( \frac{r^2}{r_0^2} + \frac{2r_0}{r} - 3 \right) r^2 dr$$

as we wanted to show. The limits of integration reflect the fact that $H' = 0$ for all $r > r_0$.

(b) To do this integral exactly is messy – but because the nuclear radius $r_0$ is so small compared to the typical scale over which $R_{n\ell}(r)$ varies ($\sim a_{\text{Bohr}}$), we can approximate the radial wave function by its value at the origin, and assume that $R_{n\ell}(r) \to R_{n\ell}(0)$ 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). Thus, our problem reduces to that of determining the value of $R_{n0}$ at the origin, $r = 0$. We can use the equations on page 152 and work out what the associated Laguerre polynomials do at the origin, or we can 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 see that $|R_{n0}(0)|^2 = 4(Z/na)^3$. With this simplification, we can now calculate the energy shift as

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

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

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

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

$$= ke^2 \frac{2}{5} \frac{r_0^2}{n^3 a_0^3} Z^4 \delta_{\ell 0}$$
3. De Generalization of De Generacy

In class, we argued that the first-order corrections to the energies of \( d \) degenerate states are given by the eigenvalues of the matrix \( H'_{ij} \), and the eigenvectors give us the “correct” set of states in the degenerate sub-space. These statements were based on working out the \( d = 2 \) case explicitly and then generalizing the results in an “obvious” way. Prove that these claims are true by considering a set of \( d \) degenerate states, \( \{ \psi^0_j \} \), that obey

\[
H^0 \psi^0_j = E^0 \psi^0_j \quad \text{with} \quad \langle \psi^0_i | \psi^0_j \rangle = \delta_{ij} \quad i, j = 1, 2, 3, \ldots, d
\]

In analogy with Eq. 6.17 in the text, consider the linear combinations

\[
\psi^0 = \sum_{j=1}^{d} \alpha_j \psi^0_j
\]

Now follow the steps in section 6.2.1 to arrive at the generalized form of Eq. 6.22:

\[
\sum_{i=1}^{d} H'_{ji} \alpha_i = E^1 \alpha_j \quad \text{where} \quad H'_{ji} \equiv \langle \psi^0_j | H' | \psi^0_i \rangle
\]

**SOLUTION**

This problem is largely an exercise in linear algebra and keeping track of indices, but it is useful to do. Starting with our set of \( d \) orthonormalized states \( \{ \psi^0_j \} (j = 1, 2, \ldots, d) \), each of which is an eigenstate of the unperturbed Hamiltonian \( H^0 \) with eigenvalue \( E^0 \), we form linear combinations

\[
\psi^0 = \sum_{j=1}^{d} \alpha_j \psi^0_j
\]

These functions are obviously also eigenstates of \( H^0 \), because

\[
H^0 \psi^0 = \sum_{j=1}^{d} \alpha_j H^0 \psi^0_j = E^0 \sum_{j=1}^{d} \alpha_j \psi^0_j = E^0 \psi^0
\]

We now want to solve the Schrödinger Equation for the perturbed system, \( H \psi = E \psi \), where \( H = H^0 + H' \). As before, we do so by expanding both the eigenvalue \( E \) and the perturbed eigenfunction \( \psi \) as power series in \( \lambda \), where the power of \( \lambda \) indicates the order of the correction. We put these expansions in the full Schrödinger Equation and collect all terms of the same power in \( \lambda \). Terms that are of order \( \lambda^0 \) give us the unperturbed eigenvalue equation, so that equality is satisfied. Collecting terms of order \( \lambda^1 \) yields the expression

\[
H^0 \psi^1 + H' \psi^0 = E^0 \psi^1 + E^1 \psi^0
\]
This is just Eq. [6.21] in the text, so we’re almost there! For our next step, we take one member of our set of degenerate states and multiply the above on the left by its complex conjugate, then integrate over all space. In Dirac notation, this means we take the inner product of the above with $\langle \psi_j^0 |$, which gives us

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

We now use one of our standard techniques, and note that due to the hermiticity of $H^0$, it can also act to the left, on $\psi_j^0$, which pulls out a factor of $E^0$. The first term on the left therefore exactly cancels the first term on the right, and so we just have

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

Our last step is to replace $| \psi^0 \rangle$ on each side of the above equality with its expansion in terms of $\{ \psi_j^\ell \}$. Pulling the expansion coefficients outside the bra-kets, the above becomes

$$
\sum_{\ell=1}^{d} \alpha_\ell \langle \psi_j^0 | H' | \psi_\ell^0 \rangle = E^1 \sum_{\ell=1}^{d} \alpha_\ell \langle \psi_j^0 | \psi_\ell^0 \rangle = E^1 \sum_{\ell=1}^{d} \alpha_\ell \delta_{j\ell} = E^1 \alpha_j
$$

where we used the orthogonality of the $\{ \psi_j^0 \}$. If we define the matrix element

$$
H'_{j\ell} \equiv \langle \psi_j^0 | H' | \psi_\ell^0 \rangle
$$

then we can rewrite the previous expression in its final form as

$$
\sum_{\ell=1}^{d} H'_{j\ell} \alpha_\ell = E^1 \alpha_j
$$

At one level, the above is just a set of $d$ coupled linear equations, that is, one equation for each value of $j$. Squinting only slightly, however, we recognize this as an eigenequation for the matrix $H'$ expressed (or represented) in the set of degenerate basis states $\{ \psi_j^0 \}$. Solving this will yield the complete set of first-order energy corrections $E^1_k$ (for $k = 1, 2, 3, \ldots, d$) as the eigenvalues, and also give us the complete set of “correct” states (appropriate linear combinations of the $\{ \psi_j^0 \}$) as the eigenfunctions.