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Contents

1 Problem #1: Anharmonic Oscillator.

Consider the anharmonic oscillator in one dimension with the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega_0^2\hat{x}^2 + \lambda\hat{x}^4 \tag{1}$$

1.1 Zero Point Energy Shift.

Calculate the change in the zero point energy resulting from the anharmonic term in the Hamiltonian to leading order in λ.

Given the perturbation $\hat{V}' = \lambda\hat{x}^4$, the shift in the zero-point energy (ground state) is

$$\delta E_0 = \lambda \langle n|\hat{x}^4|0\rangle \ , \tag{2}$$

which in the coordinate representation is

$$\delta E_0 = \sqrt{\frac{m\omega_0}{\pi\hbar}}\lambda \int_{-\infty}^{\infty} x^4 \left(e^{-m\omega_0 x^2/2\hbar}\right)^2 = \sqrt{\frac{c}{\pi}}\lambda\frac{3}{4}\sqrt{\frac{\pi}{c^5}} \ , \tag{3}$$

with $c = m\omega_0/\hbar$. Note we will be using primes to denote perturbed quantities. This yields the result

$$\delta E_0 = \frac{3\lambda\hbar^2}{4m^2\omega_0^2} \quad \Rightarrow \quad E_0' = \frac{1}{2}\hbar\omega_0 + \frac{3\lambda\hbar^2}{4m^2\omega_0^2} \ . \tag{4}$$

For this potential to be solved using perturbation theory, the energy imparted by the perturbation must be negligible compared to the energy of the state. In this case, for the ground state,

$$\lambda \ll \frac{2}{3}\frac{\omega_0^3 m^2}{\hbar} \ , \tag{5}$$

for the potential to be considered a perturbation.

1.2 R.M.S. Vibrational Amplitude.

Calculate the change in the r.m.s. vibrational amplitude, *i.e.*, $\Delta x_{rms} = \langle 0|x^2|0\rangle^{1/2}$, also to leading order in λ.

To determine the new r.m.s. vibrational amplitude of the ground state, we first must determine the new ground-state wave functions ψ_0'. In the energy basis, the perturbed ground state is

$$\psi_0' \equiv |0'\rangle = |0\rangle + \sum_{n\neq 0}\frac{\langle n|\lambda\hat{x}^4|0\rangle}{E_0 - E_n}|n\rangle = |0\rangle - \frac{\lambda}{\hbar\omega_0}\left(\frac{\hbar}{2m\omega_0}\right)^2 \sum_{n=1}^{\infty}\frac{\langle n|(\hat{a}^\dagger + \hat{a})^4|0\rangle}{n}|n\rangle \ . \tag{6}$$

We can expand the operator, yielding

$$\begin{aligned}\langle n|(\hat{a}^\dagger + \hat{a})^4|0\rangle = {} & \langle n|(\hat{a}^\dagger)^4|0\rangle + \langle n|\hat{a}^\dagger\hat{a}(\hat{a}^\dagger)^2|0\rangle + \langle n|\hat{a}(\hat{a}^\dagger)^3|0\rangle + \langle n|\hat{a}^2(\hat{a}^\dagger)^2|0\rangle \\ & + \langle n|(\hat{a}^\dagger)^2\hat{a}\hat{a}^\dagger|0\rangle + \langle n|\hat{a}^\dagger\hat{a}^2\hat{a}^\dagger|0\rangle + \langle n|\hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger|0\rangle + \langle n|\hat{a}^3\hat{a}^\dagger|0\rangle \\ & + \langle n|(\hat{a}^\dagger)^3\hat{a}|0\rangle + \langle n|\hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a}|0\rangle + \langle n|\hat{a}(\hat{a}^\dagger)^2\hat{a}|0\rangle + \langle n|\hat{a}^2\hat{a}^\dagger\hat{a}|0\rangle \\ & + \langle n|(\hat{a}^\dagger)^2\hat{a}^2|0\rangle + \langle n|\hat{a}^\dagger\hat{a}^3|0\rangle + \langle n|\hat{a}\hat{a}^\dagger\hat{a}^2|0\rangle + \langle n|\hat{a}^4|0\rangle \ ,\end{aligned}$$

which reduces significantly if we note some important facts. First, any inner product where the right-most operator is the annihilation operator, will destroy the ground state, and each of those inner products is zero: $\hat{A}\hat{a}\,|0\rangle = 0$, where $\hat{A}$ is any product of creation and annihilation operators. Additionally, any remaining inner products are zero if there are the same number of creation and annihilation operators, because the final state will again be the ground state. Since the sum never has $n = 0$, the inner product $\langle n|0\rangle = 0$. This leaves us with four surviving terms (1,2,3,5 in the above expression):

$$\langle n|(\hat{a}^\dagger + \hat{a})^4|0\rangle = \langle n|(\hat{a}^\dagger)^4|0\rangle + \langle n|\hat{a}^\dagger\hat{a}(\hat{a}^\dagger)^2|0\rangle + \langle n|\hat{a}(\hat{a}^\dagger)^3|0\rangle + \langle n|(\hat{a}^\dagger)^2\hat{a}\hat{a}^\dagger|0\rangle \tag{7}$$

$$= 2\sqrt{6}\,\langle n|4\rangle + 2\sqrt{2}\,\langle n|2\rangle + 3\sqrt{2}\,\langle n|2\rangle + \sqrt{2}\,\langle n|2\rangle \ , \tag{8}$$

so each inner product is nonzero for only one value of n. Therefore, the perturbed ground state has a wave function given by

$$|0'\rangle = |0\rangle - \frac{\lambda\hbar}{4m^2\omega_0^3}\left[\frac{6\sqrt{2}}{2}\,|2\rangle + \frac{2\sqrt{6}}{4}\,|4\rangle\right] = |0\rangle - \alpha\,|2\rangle - \beta\,|4\rangle \ , \tag{9}$$

where α and β are the respective constants.

We may now find the vibrational amplitude in a similar fashion:

$$\Delta x'_{rms} = \langle 0'|\hat{x}^2|0'\rangle^{1/2} = \sqrt{\frac{\hbar}{2m\omega_0}}\left[\langle 0'|(\hat{a}^\dagger)^2|0'\rangle + \langle 0'|\hat{a}\hat{a}^\dagger|0'\rangle + \langle 0'|\hat{a}^\dagger\hat{a}|0'\rangle + \langle 0'|\hat{a}^2|0'\rangle\right]^{1/2} \ . \tag{10}$$

Let us carry out the indicated operations on $|0'\rangle$:

$$\begin{aligned}
&(\hat{a}^\dagger)^2\,|0\rangle - \alpha(\hat{a}^\dagger)^2\,|2\rangle - \beta(\hat{a}^\dagger)^2\,|4\rangle \\
&+ \hat{a}\hat{a}^\dagger\,|0\rangle - \alpha\hat{a}\hat{a}^\dagger\,|2\rangle - \beta\hat{a}\hat{a}^\dagger\,|4\rangle \\
&+ \hat{a}^\dagger\hat{a}\,|0\rangle - \alpha\hat{a}^\dagger\hat{a}\,|2\rangle - \beta\hat{a}^\dagger\hat{a}\,|4\rangle \\
&+ \hat{a}^2\,|0\rangle - \alpha\hat{a}^2\,|2\rangle - \beta\hat{a}^2\,|4\rangle \ ,
\end{aligned}$$

we can discard any terms that result in states that are not $|0\rangle\,,\ |2\rangle\,,\ |4\rangle$ because we will be taking the inner product with $|0'\rangle$. Additionally terms where $\hat{a}$ acts first on $|0\rangle$ are zero. This leaves the result

$$\begin{aligned}
(\Delta x'_{rms})^2 = \left(\sqrt{\frac{\hbar}{2m\omega_0}}\right)^2 \langle 0'|\Big[&\sqrt{2}\,|2\rangle - \alpha\sqrt{12}\,|4\rangle + |0\rangle - \alpha(3)\,|2\rangle - \beta(5)\,|4\rangle \\
&- \alpha(2)\,|2\rangle - \beta(4)\,|4\rangle - \alpha\sqrt{2}\,|0\rangle - \beta\sqrt{12}\,|2\rangle\Big] \ ,
\end{aligned}$$

collecting terms we have

$$\frac{\hbar}{2m\omega_0}\left[\langle 0| - \alpha\,\langle 2| - \beta\,\langle 4|\right]\Big[(1-\sqrt{2}\alpha)\,|0\rangle + (\sqrt{2} - 5\alpha - 2\sqrt{3}\beta)\,|2\rangle - (2\sqrt{3}\alpha + 9\beta)\,|4\rangle\Big] \ . \tag{11}$$

Finally, we get the value of the perturbed r.m.s. vibrational amplitude of the ground state:

$$\Delta x'_{rms} = \sqrt{\frac{\hbar}{2m\omega_0}}\sqrt{(1-\sqrt{2}\alpha) - \alpha(\sqrt{2} - 5\alpha - 2\sqrt{3}\beta) + \beta(2\sqrt{3}\alpha + 9\beta)} \tag{12}$$

$$= \sqrt{\frac{\hbar}{2m\omega_0}}\sqrt{1 - 2\sqrt{2}\alpha + 5\alpha^2 + 4\sqrt{3}\alpha\beta + 9\beta^2} \ . \tag{13}$$

which after plugging in for α and β gives the result

$$\Delta x'_{rms} = \frac{1}{8}\sqrt{\frac{\hbar}{m^5\omega_0^7}\left(279\lambda^2\hbar^2 + 32m^4\omega_0^6 - 96\lambda m^2\omega_0^3\hbar\right)}\ , \tag{14}$$

which to leading order in λ, is

$$\Delta x'_{rms} \simeq \sqrt{\frac{\hbar}{2m^3\omega_0^4}\left(m^2\omega_0^3 - 3\lambda\hbar\right)}\ . \tag{15}$$

Dimensionally, the right hand side has units of inverse length, which does not match the right hand side.

1.3 Energy Level Spacing.

Calculate the energy level spacing between the ground-state ($n = 0$) and first excited state ($n = 1$) and compare with the level spacing between the $n = 1$ and $n = 2$ levels, again to leading order in λ.

Let us calculate the shifts for the first and second excited states. We will follow similar logic for calculating matrix elements (and discarding when appropriate) as in the previous section:

$$\delta E_n = \lambda\left\langle n|\hat{x}^4|n\right\rangle = \lambda\left(\frac{\hbar}{2m\omega_0}\right)^2\left\langle n|(\hat{a}^\dagger + \hat{a})^4|n\right\rangle\ , \tag{16}$$

let us begin by noting that only terms with two of each operator will survive. If the number of times the state is raised is not equal to the number of times it is lowered, the resultant state will be orthogonal to the original state, and the inner product is zero. Additionally, for the first excited state, if the operator has two annihilation operators on the right hand side, the state is killed: $\hat{A}\hat{a}^2\left|1\right\rangle = 0$. Selecting the correct terms from the expression at the end of page two yields the result

$$\delta E_1 = \lambda\left(\frac{\hbar}{2m\omega_0}\right)^2(2+6+2+1+4)\left\langle 2|2\right\rangle = \frac{15}{4}\frac{\lambda\hbar^2}{m^2\omega_0^2} \tag{17}$$

$$\delta E_2 = \lambda\left(\frac{\hbar}{2m\omega_0}\right)^2(2+6+12+6+4+9)\left\langle 4|4\right\rangle = \frac{39}{4}\frac{\lambda\hbar^2}{m^2\omega_0^2}\ . \tag{18}$$

We can now see the energies of the three lowest states of the one-dimensional anharmonic oscillator:

$$E'_0 = \frac{1}{2}\hbar\omega_0 + \frac{3}{4}\frac{\lambda\hbar^2}{m^2\omega_0^2} \tag{19}$$

$$E'_1 = \frac{3}{2}\hbar\omega_0 + \frac{15}{4}\frac{\lambda\hbar^2}{m^2\omega_0^2} \tag{20}$$

$$E'_2 = \frac{5}{2}\hbar\omega_0 + \frac{39}{4}\frac{\lambda\hbar^2}{m^2\omega_0^2}\ , \tag{21}$$

and the energy spacing is

$$\Delta_{10} = \hbar\omega_0 + 3\frac{\lambda\hbar^2}{m^2\omega_0^2} \tag{22}$$

$$\Delta_{21} = \hbar\omega_0 + 6\frac{\lambda\hbar^2}{m^2\omega_0^2}\ . \tag{23}$$

It is interesting to carry out the calculation done at the end of section 1.1, to see how large the parameter λ can be to be considered a perturbation. For the $n = 2$ state, this is

$$\lambda \ll \frac{2}{5}\frac{\omega_0^3 m^2}{\hbar} \ , \tag{24}$$

and for the $n = 2$ this is

$$\lambda \ll \frac{10}{39}\frac{\omega_0^3 m^2}{\hbar} \ . \tag{25}$$

Clearly the coefficients are monotonically decreasing, so at higher and higher energy levels, the parameter λ must get increasingly small for it to be a perturbation. For a fixed, albeit small value of λ, the perturbation expansion will always break down at a large enough energy level. This makes sense, because higher energy states have access to a larger range of x, so at large values of x, regardless of how small λ is, the quartic term dwarfs the quadratic term.

2 Problem #2: Potential from Classical Proton Radius.

Assume the proton is a sphere of uniform charge density with radius, $R = 1$ fm ($1\text{fm} = 10^{-13}$ cm). Show that the electrostatic potential energy of the electron in the Coulomb field of the proton is

$$V = \begin{cases} -\frac{e^2}{R}\left[\frac{3}{2} - \frac{1}{2}\frac{r^2}{R^2}\right] & r < R \\ -\frac{e^2}{r} & r > R \end{cases} . \tag{26}$$

Calculate the shift in the ground state energy of Hydrogen that results from "smearing" the proton charge uniformly over the radius of the proton. Is this shift significant compared to the leading relativistic corrections of order $\alpha^4 m_e c^2$?

It is easy to see that outside the proton, the electrostatic potential is that of a point charge. We can determine the potential inside the proton using Gauss' law. The proton has charge e distributed evenly throughout its classical volume, so the charge enclosed by a sphere of radius $r < R$ is $Q_{\text{enc}} = er^3/R^3$. Gauss's law then says:

$$\int_S \mathbf{E} \cdot \mathrm{d}\mathbf{A} = \frac{Q_{\text{enc}}}{\epsilon_0} \quad \Rightarrow \quad 4\pi\epsilon_0(Er^2) = e\frac{r^3}{R^3} , \tag{27}$$

therefore in Gaussian units, the electric field is then $E = er/R^3$ inside the proton's classical radius. The line integral of the electric field gives the potential difference at two locations. Compare the potential at the surface to a point inside:

$$\phi(r) - \phi_R = -\int_R^r \mathbf{E} \cdot \mathrm{d}\boldsymbol{\ell} = \frac{e}{R^3}\int_r^R r\mathrm{d}r = \frac{e}{2R^3}(R^2 - r^2) . \tag{28}$$

The potential at the surface is simply Q/R, so we see

$$\phi(r) = \frac{e}{R}\left[\frac{1}{2}\left(1 - \frac{r^2}{R^2}\right) + 1\right] , \tag{29}$$

and the potential energy is simply the charge of the electron times the electrostatic potential:

$$V(r < R) = -\frac{e^2}{2R}\left(3 - \frac{r^2}{R^2}\right) . \tag{30}$$

We can now write the Hamiltonian for the electron in the region inside the classical radius of the proton as

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{2R}\left(3 - \frac{r^2}{R^2}\right) , \tag{31}$$

but for it to be in the form of which perturbation theory applies: $H = \hat{p}^2/(2m) + V + V'$, where V is the coulomb potential, we see the perturbation must be

$$V' = \left[\frac{e^2}{r} - \frac{e^2}{2R}\left(3 - \frac{r^2}{R^2}\right)\right]\Theta(r - R) , \tag{32}$$

where $\Theta(x)$ is the Heaviside step function. The whole Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{r} + \left[\frac{e^2}{r} - \frac{e^2}{2R}\left(3 - \frac{r^2}{R^2}\right)\right]\Theta(R - r) . \tag{33}$$

The shift to the ground state energy of the electron in the Hydrogen atom due to this perturbation is

$$\delta E_0 = \frac{1}{\pi a_0^3} \langle e^{-r/a_0} | \left[\frac{e^2}{r} - \frac{e^2}{2R} \left(3 - \frac{r^2}{R^2} \right) \right] \Theta(r-R) | e^{-r/a_0} \rangle \ , \tag{34}$$

explicitly writing out the integrals yields

$$\delta E_0 = \frac{1}{\pi a_0^3} \left[e^2 \int_0^R \frac{e^{-2r/a_0}}{r} \mathrm{d}V - \frac{3e^2}{2R} \int_0^R e^{-2r/a_0} \mathrm{d}V + \frac{e^2}{2R^3} \int_0^R r^2 e^{-2r/a_0} \mathrm{d}V \right] \ , \tag{35}$$

with $\mathrm{d}V = 4\pi r^2 \mathrm{d}r$. The integrals are

$$\int_0^R e^{-2r/a_0} r \mathrm{d}r = \frac{1}{4} a_0 \left(a_0 - e^{-\frac{2R}{a_0}} \left(a_0 + 2R \right) \right) \tag{36}$$

$$\int_0^R e^{-2r/a_0} r^2 \mathrm{d}r = \frac{1}{4} a_0 \left(a_0^2 - e^{-\frac{2R}{a_0}} \left(2a_0 R + a_0^2 + 2R^2 \right) \right) \tag{37}$$

$$\int_0^R e^{-2r/a_0} r^4 \mathrm{d}r = \frac{3a_0^5}{4} - \frac{1}{4} a_0 e^{-\frac{2R}{a_0}} \left(a_0 \left(3a_0 \left(2a_0 R + a_0^2 + 2R^2 \right) + 4R^3 \right) + 2R^4 \right) \ , \tag{38}$$

plugging these back in to Equation 35 yields

$$\delta E_0 = \frac{e^2}{2a_0 R^3} \left[2R^3 + 3a_0 \left(a_0 + R \right) \left(a_0 - R - e^{-\frac{2R}{a_0}} \left(a_0 + R \right) \right) \right] \tag{39}$$

$$= \frac{e^2}{2a_0 R^3} \left[2R^3 - 3a_0 R^2 + 3a_0^3 - 3a_0 e^{-\frac{2R}{a_0}} \left(a_0 + R \right)^2 \right] \ , \tag{40}$$

after inserting the values $a_0 = 5.29\text{e}{-9}$ cm and $e = 4.8\text{e}{-10}$ esu, and the classical radius of the electron the value of the shift in the ground state energy is

$$\delta E_0 = 1.197\,34\text{e}{-12} \text{ ergs} = 0.747 \text{ eV} \ , \tag{41}$$

which we can compare to the relativistic correction

$$\delta E_{\text{rel}} = \alpha^4 m_e c^2 = 2.32\text{e}{-15} \text{ ergs} = 1.45\text{e}{-3} \text{ eV} \ , \tag{42}$$

and see the correction due to smearing the charge along the "surface" of the proton is much larger than the relativistic correction. I believe this is due to MATHEMATICA having difficulties with such small numbers. Consider an aprroximation to this expression, below.

The integrals could have been approximated: for $r < R$, $R \ll a_0$, so $e^{-r/a_0} \sim 1$, so Equation 35 becomes

$$\delta E_0 \simeq \frac{4e^2}{a_0^3} \int_0^R \left[r - \frac{3}{2R} r^2 + \frac{1}{2R^3} r^4 \right] \mathrm{d}r = \frac{4e^2}{a_0^3} \left(\frac{R^2}{10} \right) = \frac{2}{5} \frac{e^2 R^2}{a_0^3} = 3.89\text{e}{-9} \text{ eV} \ , \tag{43}$$

which is a few orders of magnitude off from the exact answer, but still small compared to the relativistic correction. This makes more sense than the solution given in Equation 41.

3 Problem #3: Hydrogen Atoms in Electric Field.

Hydrogen atoms, originally in their ground state, are placed in a uniform electric field $E = \mathscr{E}\hat{\mathbf{z}}$. Derive an expression for the induced electric dipole moment, $\langle \mathbf{P} \rangle = \langle \psi_0 | (-e\mathbf{r}) | \psi_0 \rangle$, of the ground state of hydrogen that is valid to leading order in the electric field. Specify precisely which matrix elements contribute to the dipole moment. Construct upper and lower bounds for the dipole moment.

To begin, we must calculate the shift of the ground state wave function due to this perturbation, which involves calculating the matrix elements

$$V_{n\ell m} = \langle n\ell m | e\mathscr{E}\hat{z} | 100 \rangle \ , \tag{44}$$

which in the coordinate representation is

$$V_{1n\ell m} = e\mathscr{E} \int_0^\infty \int_0^\pi \int_0^{2\pi} (r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi)(r\cos\theta) R^*_{n\ell}(r) R_{10}(r) Y_0^0(\theta,\phi) Y_\ell^{m*}(\theta,\phi) \ , \tag{45}$$

where

$$R_{n\ell}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^\ell L^{2\ell+1}_{n-\ell-1}(2r/na_0) \ , \tag{46}$$

with the generalized Laguerre polynomials denoted by L. We can exploit the orthogonality of the spherical harmonics by noting that $Y_0^0 \cos\theta = Y_1^0/\sqrt{3}$, which makes the integral

$$\begin{aligned} V_{n\ell m} &= \frac{e\mathscr{E}}{\sqrt{3}} \int_0^\infty (r^3 \mathrm{d}r) R^*_{n\ell}(r) R_{10}(r) \int_0^\pi \int_0^{2\pi} Y_1^0(\theta,\phi) Y_\ell^{m*}(\theta,\phi) \sin\theta \mathrm{d}\theta\mathrm{d}\phi & (47) \\ &= \frac{e\mathscr{E}}{\sqrt{3}} \delta_{1\ell}\delta_{0m} \int_0^\infty (r^3\mathrm{d}r) R^*_{n\ell}(r) R_{10}(r) \ , & (48) \end{aligned}$$

we note this yields the selection rules $\Delta\ell = \pm 1$ and $\Delta m_\ell = 0$. So the perturbed ground state wave function, to first order, is

$$|0'\rangle = |0\rangle + \sum_{n=1}^\infty \frac{\langle n10 | e\mathscr{E} z | 100 \rangle}{E_1 - E_n} |n10\rangle \ , \tag{49}$$

where $E_n = E_1/n^2$ where E_1 is the Rydberg constant. The induced dipole moment is given by

$$\langle \mathbf{P} \rangle = \langle 0' | (-e\mathbf{r}) | 0' \rangle = -e \langle 0' | r\cos\phi\sin\theta\mathbf{i} + r\sin\phi\sin\theta\mathbf{j} + r\cos\theta\mathbf{k} | 0' \rangle \ , \tag{50}$$

where $|0'\rangle$ is the ground state $|100\rangle$. The ground state will only have contributions to the perturbation from orthogonal states with $\ell = 1$ and $m = 0$, and thus have no azimuthal dependence, so the expectation value of $\mathbf{r}$ is

$$\langle n10 | r\cos\phi\sin\theta\mathbf{i} + r\sin\phi\sin\theta\mathbf{j} + r\cos\theta\mathbf{k} | n10 \rangle = \langle n10 | r\cos\theta | n10 \rangle \, \mathbf{k} \ , \tag{51}$$

because the azimuthal functions were integrated over a full period $\phi = [0, 2\pi]$, so they are zero. This also shows that because the ground state has no polar dependence either, the z integral is zero as well and $\langle 0 | r\cos\theta | 0 \rangle$, where $|0\rangle$ is the unperturbed ground state. We can now expand Equation 50,

$$\frac{\langle \mathbf{P} \rangle}{-e} = \left[\langle 100 | + \sum_{n=1}^\infty \frac{\langle 100 | e\mathscr{E} z | n10 \rangle}{E_1 - E_n} \langle n10 | \right] |z| \left[|100\rangle + \sum_{n=1}^\infty \frac{\langle n10 | e\mathscr{E} z | 100 \rangle}{E_1 - E_n} |n10\rangle \right] \ , \tag{52}$$

which results in four terms, the last of which is the inner product of two infinite sums. This term will be ignored because it is second order in the electric field, which is assumed to be small for the perturbation expansion to be valid. The expression above is then

$$\frac{\langle \mathbf{P} \rangle}{-e} = \langle 100|e\mathscr{E}z|100\rangle + \sum_{n=1}^{\infty} \frac{\langle 100|e\mathscr{E}z|n10\rangle}{E_1 - E_n} \langle n10|z|100\rangle + \sum_{n=1}^{\infty} \frac{\langle n10|e\mathscr{E}z|100\rangle}{E_1 - E_n} \langle 100|z|n10\rangle \ , \quad (53)$$

so the induced dipole moment is

$$\langle \mathbf{P} \rangle = -2e^2\mathscr{E} \sum_{(n\ell m_\ell)'} \frac{|\langle n\ell m_\ell|z|100\rangle|^2}{E_1 - E_n} = -2e^2\mathscr{E} \sum_{n=1}^{\infty} \frac{|\langle n10|z|100\rangle|^2}{E_1 - E_n} \ , \quad (54)$$

note the primed sum indicates it excludes $|n\ell m_\ell\rangle = |100\rangle$. We can identify as twice the quotient of the second order correction to the ground state energy E_1 and the electric field. From here, we can follow the method used by Shankar[1] to put upper and lower bounds on the value of the induced dipole moment. We know for any $n' > 2$ the energy of the n'th state is always smaller in magnitude than the second state:

$$\begin{cases} E_2 = \frac{E_1}{2^2} \\ E_{n'} = \frac{E_1}{(n')^2} \end{cases} \qquad E_2 > E_{n'} \ \Rightarrow \ \frac{1}{4} > \frac{1}{(n')^2} \ ,$$

which is true if $n > 2$ as we claimed. This allows us to say that

$$|\langle \mathbf{P} \rangle| \leq \frac{2e^2\mathscr{E}}{|E_1 - E_2|} \sum_{n=1}^{\infty} |\langle n\ell m_\ell|z|100\rangle|^2 \ , \quad (55)$$

the sum can be written as

$$\sum_{(n\ell m_\ell)'}^{\infty} |\langle n\ell m_\ell|100\rangle|^2 = -|\langle 100|z|100\rangle|^2 + \sum_{n\ell m_\ell}^{\infty} \langle 100|z|n\ell m_\ell\rangle \langle n\ell m_\ell|z|100\rangle \ , \quad (56)$$

after pulling out the first term in the sum, which we have already shown is zero. Additionally we can see the completeness relation in the remaining term, which is simply the identity:

$$\sum_{(n\ell m_\ell)'}^{\infty} |\langle n\ell m_\ell|100\rangle|^2 = \langle 100|z^2|100\rangle = a_0^2 \ , \quad (57)$$

because the expectation value of a squared coordinate is simply the Bohr radius. The upper bound on the magnitude of the induced dipole moment is then

$$|\langle \mathbf{P} \rangle| \leq \frac{2e^2\mathscr{E}}{|E_1 - E_2|} a_0^2 = \frac{2e^2\mathscr{E}}{\frac{3}{4}(e^2/2a_0)|} a_0^2 = \frac{16\mathscr{E}a_0^3}{3} \ , \quad (58)$$

where the Rydberg constant $E_1 = e^2/2a_0$ in Gaussian units. Clearly, if we take the absolute value of the terms as done previously, each term adds to the total (and none subtract) so the total must be greater than keeping only the first term in the sum. The right-most expression of Equation 54 yields

$$|\langle \mathbf{P} \rangle| \geq 2e^2\mathscr{E} \frac{|\langle 210|z|100\rangle|^2}{E_1 - E_2} = \frac{16}{3}\mathscr{E}a_0 |\langle 210|z|100\rangle|^2 \ , \quad (59)$$

[1] Principles of Quantum Mechanics, 2^{nd} ed. pg 460.

the matrix element in the coordinate basis is

$$\langle 210|z|100\rangle = \frac{1}{\sqrt{32}\pi a_0^3}\int_0^\infty r^2 \mathrm{d}r \int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi (r\cos\theta) e^{-r/a_0}\frac{r}{a_0}e^{-r/2a_0}\cos\theta \tag{60}$$

$$= \frac{2\pi}{\sqrt{32}\pi a_0^4}\int_0^\infty r^4 e^{-\frac{3}{2}(r/a_0)}\mathrm{d}r \int_0^\pi \sin\theta(\cos\theta)^2\mathrm{d}\theta \tag{61}$$

$$= \frac{2}{2^{5/2}a_0^4}\left(\frac{2^8 a_0^5}{3^4}\right)\left(\frac{2}{3}\right) \tag{62}$$

$$|\langle 210|z|100\rangle|^2 = \frac{2^{20-5}a_0^2}{3^{10}}\ , \tag{63}$$

so the lower bound is

$$|\langle \mathbf{P}\rangle| \geq \frac{16}{3}\mathscr{E} a_0 \frac{2^{15}a_0^2}{3^{10}} = \left(\frac{2^{19}}{3^{11}}\right)\mathscr{E} a_0^3\ . \tag{64}$$