PHYS 812: Assignment 2

1. Consider the Thomas-Reiche-Kuhn sum rule

\[ \sum_{n'} (E_{n'} - E_n) |\langle n' |X| n \rangle|^2 = \frac{\hbar^2}{2m} \]

where \(|n⟩\) and \(|n'⟩\) are eigenstates of \(H = P^2/2m + V(X)\).

(a) Prove this rule. Hint: Eliminate the \((E_{n'} - E_n)\) factor in favor of \(H\).

(b) Test the sum rule on the \(n\)th state of the harmonic oscillator.

2. Consider the ground state of the hydrogen atom in a uniform electric field \(E = \hat{E} \hat{z}\).

(a) Show that an operator \(\Omega\) defined in position space as \(\Omega = -(ma_0eE/\hbar^2)(rz/2 + a_0z)\), where \(m\) is the electron reduced mass, \(e\) is the magnitude of its charge, and \(a_0\) is the Bohr radius, satisfies the equation

\[ H^{(1)} |100⟩ = [\Omega, H_0] |100⟩ \]

where \(H_0\) and \(H^{(1)}\) are the unperturbed and the perturbation operators and \(|100⟩\) is the ground state wave vector.

(b) Using the properties of \(\Omega\), show that the second-order energy correction due to the perturbation \(H^{(1)}\) is \(-\langle 9/4 \rangle a_0^3 E^2\)

3. Consider the first-order correction for the \(n = 2\) level of the hydrogen atom in a constant electric field.

(a) Use the dipole selection rules to show that matrix elements of the operator \(H^{(1)} = eE Z\) in the basis of unperturbed states corresponding to \(n = 2\) are \(\langle 2l'm'|H^{(1)}|2lm⟩ = e\delta_{mm'}(\delta_{l,l-1} + \delta_{l-1,l'})\).

(b) Show that \(e = -3eEa_0\).

4. We discuss here some tricks for evaluating the expectation values of certain operators in the eigenstates of hydrogen.

(a) Suppose we want to evaluate \(\langle 1/r ⟩_{nlm}\). Consider first \(\langle \lambda/r \rangle\). We can interpret \(\langle \lambda/r \rangle\) as the first-order correction due to a perturbation \(\lambda/r\). Now this problem can be solved exactly: we just replace \(e^2\) by \(e^2 - \lambda\) everywhere. (Why?) Since the energy of the hydrogen atom is \(E_n = -me^4/(2\hbar^2 n^2)\), the exact energy of the perturbed system is \(E(\lambda) = -m(e^2 - \lambda)^2/(2\hbar^2 n^2)\). The first-order correction is the term linear in \(\lambda\), that is \(E^{(1)} = me^2 \lambda/(2\hbar^2 n^2) = \langle \lambda/r \rangle\), from which we get \(\langle 1/r \rangle = 1/a_0 n^2\). (Show this.) For later use, let us observe that as \(E(\lambda) = E^{(0)} + E^{(1)} + \cdots = E(\lambda = 0) + \lambda(dE/d\lambda)_{\lambda=0} + \cdots\), one way to extract \(E^{(1)}\) from the exact answer is to calculate \((dE/d\lambda)_{\lambda=0}\).
(b) Consider now \( \langle \lambda / r^2 \rangle \). In this case, an exact solution is possible since the perturbation just modifies the centrifugal term as follows:
\[
\frac{\hbar^2 l(l + 1)}{2mr^2} + \frac{\lambda}{r^2} = \frac{\hbar^2 l'(l' + 1)}{2mr^2}
\]
where \( l' \) is a function of \( \lambda \). When deriving the expression for \( E_n \) quoted in point (a), we first got it in the form dependent on \( l \): \(-me^4/(2\hbar^2(k + l + 1)^2)\). Therefore now the dependence of \( E \) on \( \lambda \) is
\[
E(l') = -\frac{me^4}{2\hbar^2(k + l' + 1)^2} = E(\lambda) = E^{(0)} + E^{(1)} + \cdots
\]
Show that
\[
\langle \frac{\lambda}{r^2} \rangle = E^{(1)} = \lambda \left. \frac{dE}{d\lambda} \right|_{\lambda=0} = \lambda \left. \left( \frac{dE}{dl'} \right) \right|_{l'=l} \left. \left( \frac{dl'}{d\lambda} \right) \right|_{\lambda=0} = \frac{\lambda}{n^3 a_0^2 (l + 1/2)}.
\]
(c) Consider finally \( \langle 1/r^3 \rangle \). Since there is no such term in the Coulomb Hamiltonian, we resort to another trick. Consider the radial momentum operator, \( p_r = -i\hbar(\partial/\partial r + 1/r) \), in terms of which we may write the radial part of the Hamiltonian as
\[
-\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \right) \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)
\]
as \( p_r^2/2m \). (Verify this.) Using the fact that \( \langle [H, p_r] \rangle = 0 \) in the energy eigenstates, and by explicitly evaluating the commutator, show that
\[
\langle \frac{\lambda}{r^3} \rangle = \frac{1}{a_0(l)(l + 1)} \langle \lambda \rangle
\]
combining this with the result from part (b) we get
\[
\langle \frac{1}{r^3} \rangle_{nl} = \frac{1}{l(l + 1/2)(l + 1)n^3 a_0^3}
\]
(d) Find the mean kinetic energy using the trick from part (a), this time rescaling the mass. Regain the virial theorem.