

Quantum Physics III (8.06) Spring 2006

Solution Set 6

March 17, 2006

1. The Feynman-Hellmann theorem (10 points)

(a) **(5 points)** We will prove the Feynman-Hellmann theorem two ways. First, we Taylor expand $H(\lambda+\epsilon) = \sum_{n=0}^{\infty} H^{(n)}(\lambda)\epsilon^n$. Likewise, we Taylor-expand $E_m(\lambda+\epsilon) = \sum_{n=0}^{\infty} E_m^{(n)}(\lambda)\epsilon^n$, and $\psi_m(\lambda+\epsilon) = \sum_{n=0}^{\infty} \psi_m^{(n)}(\lambda)\epsilon^n$. We then use these expansions in the identity $E_m = \langle \psi_m | H | \psi_m \rangle$ to find an infinite set of equations, matching orders in ϵ on both sides. We are interested in the $\mathcal{O}(\epsilon)$ equation, because $H^{(1)}(\lambda) = \frac{\partial H}{\partial \lambda}$. We can save ourselves some algebra, as this order-matching in ϵ is exactly the same order-matching that we did when we derived the formulas for first-order perturbation theory. Thus, it suffices to treat $\epsilon H^{(1)}$ as a perturbation. We then have

$$E_m^{(1)} = \frac{\partial E_m}{\partial \lambda} = \langle \psi_m | H^{(1)} | \psi_m \rangle = \langle \psi_m | \frac{\partial H}{\partial \lambda} | \psi_m \rangle. \quad (1)$$

Alternatively, we can consider differentiating the identity $E_m = \int dx \psi^* H \psi$ with respect to λ . This yields $\frac{\partial E_m}{\partial \lambda} = \int dx \psi_m^* \frac{\partial H}{\partial \lambda} \psi_m + E_m \frac{\partial}{\partial \lambda} \int \psi_m^* \psi_m$. Since ψ_m is normalized, we can conclude $\frac{\partial E_m}{\partial \lambda} = \int dx \psi_m^* \frac{\partial H}{\partial \lambda} \psi_m$, as we desired to show.

(b) **(5 points)** We recall $H_{sho} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m\omega^2 x^2}{2}$, and $E_{sho} = (n + \frac{1}{2})\hbar\omega$.

- We first take $\lambda = \omega$. Using (1), we have

$$(n + \frac{1}{2})\hbar = \langle n | \frac{2}{\omega} V(x) | n \rangle.$$

Multiplying by $\omega/2$ on both sides, we find

$$\frac{1}{2}E_n = \langle n | V(x) | n \rangle,$$

or $\langle V(x) \rangle = \frac{1}{2}E$.

- We now take $\lambda = \hbar$. Applying (1), we have

$$(n + \frac{1}{2})\omega = \langle n | \frac{2}{\hbar} T(x) | n \rangle.$$

Using similar algebra, we can rewrite this as $\langle T(x) \rangle = \frac{1}{2}E$.

- We now take $\lambda = m$. Equation (1) now gives us

$$0 = \frac{1}{m} \langle n | T(x) - V(x) | n \rangle,$$

or $\langle T(x) \rangle = \langle V(x) \rangle$.

According to the virial theorem, $\frac{1}{2}E = \langle T \rangle = \langle V \rangle$, which is exactly what we have derived above.

2. Energy shift due to finite nuclear size (12 points)

(a) **(3 points)** Our charge distribution is $\rho(r) = \frac{3e}{4\pi R^3}$ for $r \leq R$, and 0 for $r > R$. Using Gauss' law, we find

$$\begin{aligned} E(r) &= \frac{er}{R^3} & r < R \\ &= \frac{e}{r^2} & r \geq R \end{aligned}$$

Integrating to find the potential energy $V(r) = -e \int_r^\infty E dr$, we find

$$\begin{aligned} V(r) &= -\frac{e^2}{r} & r > R \\ &= -e^2 \left(\frac{1}{2R^3} (R^2 - r^2) + \frac{1}{R} \right) & r < R. \end{aligned}$$

(b) **(6 points)** We learned on the previous part of the problem that for $r < R$, the electrostatic potential has been modified: $V(r) = -\frac{e^2}{r} - e^2 \left[\frac{R^2 - r^2}{2R^3} + \frac{1}{R} - \frac{1}{r} \right] \equiv V_0(r) + \Delta V(r)$. We will treat ΔV as a perturbation. The first-order change in the ground state energy is $\Delta E_1^{(1)} = \langle \psi_{\text{ground}} | \Delta V | \psi_{\text{ground}} \rangle$. Using $\psi_{\text{ground}} = \frac{2}{(4\pi a_0^3)^{1/2}} e^{-r/a_0}$, this becomes

$$\Delta E_1^{(1)} = \int_0^R r^2 dr \left(-\frac{4e^2}{a_0^3} \right) e^{-2r/a_0} \left[\frac{R^2 - r^2}{2R^3} + \frac{1}{R} - \frac{1}{r} \right].$$

The integrals above *can* be done exactly, using integration by parts, iterated as necessary. However, since we are already approximating, and since $R \ll a_0$, we can make our lives easier by replacing $\psi(r)$ by $\psi(0)$ since ψ does not change rapidly in this region. Then

$$\begin{aligned} \Delta E_1^{(1)} &\simeq \left(-\frac{4e^2}{a_0^3} \right) \int_0^R dr \left[\frac{r^2(R^2 - r^2)}{2R^3} + \frac{r^2}{R} - r \right] \\ &= \frac{4e^2 R^2}{10a_0^3}. \end{aligned}$$

Plugging in numbers, $\Delta E_1^{(1)} = 3.8 \times 10^{-9}$ eV. Since $E_1^{(0)} = -\frac{e^2}{2a_0}$, the ratio of the first-order correction to the unperturbed ground state energy is

$$\frac{|\Delta E_1^{(1)}|}{|E_1^{(0)}|} = \frac{4}{5} \left(\frac{R}{a_0} \right)^2 = 2.8 \times 10^{-10},$$

which is very small.

(c) **(3 points)** The effect of finite nuclear size is most important for $l = 0$ states, as $\psi_{nl}(0) = 0$ unless $l = 0$. We can estimate the relative importance of the effect for $l = 1$ states by noting that $\psi_{n1}(r)$ contains an additional factor of r/a_0 relative to $\psi_{n0}(r)$. This means that the first-order correction to the energy for $l = 1$ has an additional factor of $(R/a_0)^2 \sim 10^{-10}$ relative to the first-order correction to the energy for $l = 0$.

3. Polarizability of a particle on a ring (18 points)

(a) **(4 points)** The unperturbed Hamiltonian $H_0 = -\frac{\hbar^2}{2ma^2} \frac{\partial^2}{\partial \phi^2}$ has (normalized) eigenfunctions $\psi_n(\phi) = \sqrt{\frac{1}{2\pi}} e^{-in\phi}$, for all integers n . The energy eigenvalues are $E_n = \frac{\hbar^2 n^2}{2ma^2}$. Since the energy depends only on n^2 , the energies E_n and E_{-n} are degenerate, so all energy levels are doubly degenerate except $n = 0$, which is non-degenerate.

(b) **(6 points)** We can use the usual non-degenerate perturbation theory to calculate the first order correction to the ground state wave function. We need the matrix elements $\langle n | \cos \phi | 0 \rangle$, where I have introduced the notation $|n\rangle \cong \sqrt{\frac{1}{2\pi}} e^{-in\phi}$. Now $\cos \phi = \frac{1}{2}(e^{i\phi} + e^{-i\phi})$, and $e^{\pm i\phi} |n\rangle = |n \pm 1\rangle$, so $\langle n | \cos \phi | 0 \rangle = \frac{1}{2}(\delta_{n,1} + \delta_{n,-1})$. Thus,

$$\psi_0^{(1)} = \frac{ma^3}{\hbar^2} q \epsilon (|1\rangle + |-1\rangle).$$

The induced electric dipole moment is $\langle \psi_0 | qa \cos \phi | \psi_0 \rangle = 2qa \langle \psi_0^{(0)} | \cos \phi | \psi_0^{(1)} \rangle$, which after some algebra we find to be

$$\vec{d}_{\text{induced}} = \frac{2ma^4 q^2}{\hbar^2} \epsilon.$$

The polarizability of the system is, therefore, $P = \frac{2ma^4 q^2}{\hbar^2}$.

(c) **(8 points)** Because there are three hydrogen atoms, if we rotate one CH_3 group by $2\pi/3$, then the overall system is left invariant. Therefore our perturbation should have a 3-fold rotation symmetry. Since that is the simplest way to make sure $H'(\phi + 2\pi/3) = H'(\phi)$. The simplest Hermitian operator we could thus write down would be $H' \propto \cos 3\phi$ (the choice $H' \propto \sin 3\phi$ only differs by a choice of origin).

The change in the ground state energy due to the perturbation $H' = b \cos 3\phi$ is to first order 0. To second order, we have

$$\begin{aligned} \Delta E_0^{(2)} &= \sum_k -\frac{2ma^2 b^2}{\hbar^2 k^2} \frac{1}{4} (\delta_{k,3} + \delta_{k,-3}) \\ &= -\frac{ma^2 b^2}{9\hbar^2}. \end{aligned}$$

The change in the ground state wave function is to first order

$$\begin{aligned} \Delta \psi_0^{(1)} &= -\frac{ma^2 b}{\hbar^2} \sum_k \frac{\delta_{k,3} + \delta_{-k,3}}{k^2} |k\rangle \\ &= -\frac{ma^2 b}{9\hbar^2} (|3\rangle + |-3\rangle). \end{aligned}$$

In position space, the ground state wave function is $\psi_0 = \sqrt{\frac{1}{2\pi}} (1 - \frac{2ma^2 b}{9\hbar^2} \cos 3\phi)$, so ψ_0 is minimized where $\cos 3\phi = 1$, and maximized where $\cos 3\phi = -1$. Thus there is a higher probability of finding the orientation of the CH_3 group at $\phi = \pi/3, \pi, 5\pi/3$, and a lower probability of finding it at $\phi = 0, 2\pi/3, 4\pi/3$. This is easy to understand physically, if we look at the ethane molecule end-on (see figure 1). The molecule can lower its energy by rotating in such a way as to minimize the electrostatic energy arising from the interaction between the hydrogen atoms in the two groups.

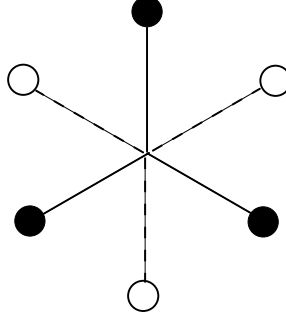


Figure 1: A cartoon of an ethane molecule in its most favorable orientation, seen end on.

4. Stark effect for $n = 3$ states of hydrogen (10 points)

(a) **(5 points)** We want to calculate $\int d^3x \psi_{3lm}^* z \psi_{3l'm'}$, while doing as little work as possible.

First, since the perturbation $H'_S = -e\varepsilon z$ is independent of ϕ , it will not connect states with different values of m , since the functions $\{e^{im\phi}\}$ are orthogonal. Therefore, $\langle 3lm|H'|3l'm'\rangle \propto \delta_{mm'}$, which we can summarize as “ $\Delta m = 0$ ”.

Second, the integral $\int d^3x \psi_{3lm}^* z \psi_{3l'm'}$ will vanish if the integral is odd under parity. The spherical harmonics Y_{lm} have parity $(-1)^l$, and z is parity-odd. Therefore, $\int d^3x \psi_{3lm}^* z \psi_{3l'm'}$ vanishes unless $l + l'$ is odd. For our case, there are two possibilities: either $l = 2$ and $l' = 1$, or $l = 1$ and $l' = 0$. We can summarize this condition as “ $\Delta l = 1$ ”.

The two above conditions have eliminated all matrix elements except $\langle 300|H'_S|310\rangle$, $\langle 31 \pm 1|H'_S|32 \pm 1\rangle$, and $\langle 310|H'_S|320\rangle$. Now we need to actually do the integrals. They are tedious but not difficult to do by hand, but we will simply quote the results: (**There is no need to evaluate c_1, c_2, c_3 explicitly to get the full credit.**)

$$\begin{aligned}\langle 300|H'_S|310\rangle &= 3\sqrt{6}a_0e\varepsilon = c_1 a_0e\varepsilon \\ \langle 310|H'_S|320\rangle &= 3\sqrt{3}a_0e\varepsilon = c_2 a_0e\varepsilon \\ \langle 31 \pm 1|H'_S|32 \pm 1\rangle &= \frac{9}{2}a_0e\varepsilon = c_3 a_0e\varepsilon\end{aligned}$$

(b) **(5 points)** In the basis $\{|300\rangle, |310\rangle, |320\rangle, |311\rangle, |321\rangle, |31-1\rangle, |32-1\rangle, |322\rangle, |32-2\rangle\}$, the matrix representation of H'_S in the degenerate subspace is

$$H'_S = 3a_0e\varepsilon \begin{pmatrix} 0 & \sqrt{6} & 0 & & & & & & \\ \sqrt{6} & 0 & \sqrt{3} & & & & & & \\ 0 & \sqrt{3} & 0 & & & & & & \\ & & & 0 & \frac{3}{2} & & & & \\ & & & \frac{3}{2} & 0 & & & & \\ & & & & & 0 & \frac{3}{2} & & \\ & & & & & \frac{3}{2} & 0 & & \\ & & & & & & & 0 & \\ & & & & & & & & 0 \end{pmatrix}.$$

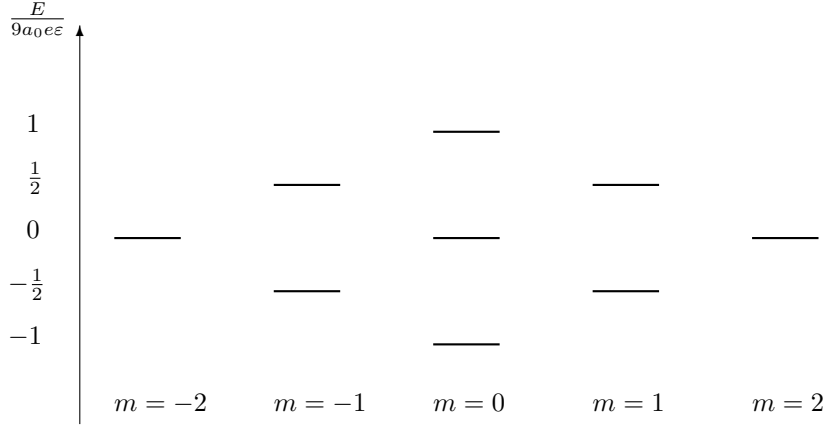


Figure 2: A sketch of the Stark effect on the $n = 3$ energy levels of hydrogen

(Anything not explicitly filled in above is zero.) This matrix is block-diagonal, so we can diagonalize each block separately.

The first block, the three-by-three matrix in the upper left-hand corner, has eigenvalues $\lambda = 0, \pm 3$. This gives the first order correction to the energy eigenvalues as $\Delta E_S^{(1)} = 0, \pm 9a_0 e \epsilon$ (or $\Delta E_S^{(1)} = 0, \pm \sqrt{c_1^2 + c_2^2} a_0 e \epsilon$).

The second and third blocks, the two-by-two blocks, have eigenvalues $\lambda = \pm \frac{3}{2}$. The first order corrections in these blocks are $\Delta E_S^{(1)} = \pm \frac{9}{2} a_0 e \epsilon$ (or $\Delta E_S^{(1)} = \pm c_3 a_0 e \epsilon$). Both of these eigenvalues are twofold degenerate.

The final two eigenvalues are clearly both 0, so the eigenvalue 0 is threefold degenerate in total.

We now need to show that the eigenstates of H'_S are also eigenstates of L_z . This is easy: as we already noted, H'_S does not depend on ϕ . Therefore, it commutes with $L_z = \hbar \frac{\partial}{\partial \phi}$, and the two operators are simultaneously diagonalizable.

Noting that each block of H'_S has the same L_z eigenvalue m_l , we can draw our energy level diagram; see figure 2.