Quantum Physics III (8.06) Spring 2008
Solution Set 6

March 18, 2008

1. **The Feynman-Hellmann theorem (12 points)**

   (a) **(6 points)**

   Consider differentiating the identity

   $$E_m = \langle\psi_m|H|\psi_m\rangle$$

   with respect to λ. This yields

   $$\begin{aligned}\frac{\partial E_m}{\partial\lambda} &= \langle\psi_m|\frac{\partial H}{\partial\lambda}|\psi_m\rangle + \langle\frac{\partial\psi_m}{\partial\lambda}|H|\psi_m\rangle + \langle\psi_m|H|\frac{\partial\psi_m}{\partial\lambda}\rangle &(1)\\ &= \langle\psi_m|\frac{\partial H}{\partial\lambda}|\psi_m\rangle + E_m\frac{\partial}{\partial\lambda}\langle\psi_m|\psi_m\rangle &(2)\\ &= \langle\psi_m|\frac{\partial H}{\partial\lambda}|\psi_m\rangle &(3)\end{aligned}$$

   where we have used that ψ_m is normalized $\implies \langle\psi_m|\psi_m\rangle = 1$. The above derivation applies to any Hermitian operator and its eigenvalues.

   (b) **(6 points)** We recall that for a simple harmonic oscillator, the Hamiltonian is $H = T(x) + V(x)$, where $T(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ and $V(x) = \frac{m\omega^2x^2}{2}$, and its eigenvalues are $E_n = (n+\frac{1}{2})\hbar\omega$.

   - We first take $\lambda = \omega$. Using (3), 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 (3), 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 (3) 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 (14 points)**

(a) **(4 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 the radial component of the Electric field to be

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

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

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

(b) **(7 points)** We learned on the previous part of the problem that for $r < R$, the electrostatic potential has been modified: $V(r) = -\frac{e^2}{r} - e^2[\frac{R^2-r^2}{2R^3} + \frac{1}{R} - \frac{1}{r}] \equiv V_0(r) + \Delta V(r)$. We will treat ΔV as a perturbation. The first-order change in the ground state energy is $\Delta E_1^{(1)} = \langle\psi_{ground}|\Delta V|\psi_{ground}\rangle$. Using $\psi_{ground} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$ ($a_0 = 5.3 \times 10^{-9}$ cm), 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

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

Plugging in numbers, $\Delta E_1^{(1)} = 3.8 \times 10^{-9}\,\text{eV}$. 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 the most important difference between $\psi_{n1}(r)$ and $\psi_{n0}(r)$ is 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. **Stark effect (16 points)**

(a) Using first order perturbation theory, the correction to ground state energy is given by

$$\Delta E_1^{(1)} = eE_{ext}\langle 100|z|100\rangle = eE_{ext}\int d^3x\,|\psi_{100}|^2 z = 0 \tag{4}$$

The last equality is due to that $|\psi_{100}|^2$ is symmetric under $z \to -z$.

(b) The $n = 2$ states are 4-fold degenerate (we ignore spin in this problem). Since

$$[L_z, H'_S] = 0, \qquad H'_S = eE_{ext}z$$

using the lemma proved in lecture (p.28 of the class notes), we conclude that

$$\langle nlm|H'_S|nl'm'\rangle \propto \delta_{mm'} \tag{5}$$

Also note that

$$\langle nlm|H'_S|nlm\rangle = eE_{ext}\langle nlm|z|nlm\rangle = 0 \tag{6}$$

since $|\psi_{nlm}|^2$ is symmetric under $z \to -z$. Ordering the 4 degenerate states as

$$|200\rangle, \quad |210\rangle, \quad |211\rangle, \quad |21-1\rangle$$

and using (5) and (6), then the matrix for H'_S in this degenerate subspace should have the form

$$H'_S = \begin{pmatrix} 0 & c & 0 & 0 \\ c & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{7}$$

with

$$c = \langle 200|H'_S|210\rangle = eE_{ext}\langle 200|z|210\rangle = eE_{ext}\int d^3x\,\psi^*_{200} z \psi_{210} = -3eE_{ext}a_0 \tag{8}$$

where a_0 is the Bohr radius. The eigenvalues of (7) give us the first order shifts in the energy: $-3ea_0E_{ext}, 3ea_0E_{ext}, 0, 0$. So $n = 2$ levels split into three levels: $E_2^{(0)} \pm 3ea_0E_{ext}$ and $E_2^{(0)}$ (2-fold degenerate).

(c) The eigenvectors of H'_S give us the correct un-perturbed wave functions. The eigenvectors corresponding to the eigenvalues in (b), in that order, are:

$$|1\rangle = \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle), \quad |2\rangle = \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle), \quad |3\rangle = |211\rangle, \quad |4\rangle = |21-1\rangle \tag{9}$$

Using (8) and (6), the electric dipole moment in the above states are given by

$$\langle 1|p_{e,z}|1\rangle = 3ea_0, \quad \langle 2|p_{e,z}|2\rangle = -3ea_0, \quad \langle 3|p_{e,z}|3\rangle = \langle 4|p_{e,z}|4\rangle = 0 \tag{10}$$

with $p_{e,z} = -ez$. All other components of $\vec{p}_e$ are zero in all states due to a similar symmetry argument as in (6).

4. **Van der Waals Interaction (18 points)**

[Note: The errors in Griffiths pointed out below only appear in an earlier printing of Griffiths.]

(a) **(4 points)** In cgs units we replace the factor of $4\pi\epsilon_0$ by 1. Construction of H' is quite straight forward. Each term corresponds to coulombic interactions between four possible pairs of particles. There are two attractive terms and two repulsive. [Note: Eqn. (6.97) and figure 6.14 are not in agreement. To do this, one can either interchange x_1 and x_2 in figure 6.14 or replace x_1 and x_2 by $-x_1$ and $-x_2$ respectively in eqn (6.97). However it really does not change anything that subsequently follows as all the epressions obtained are invariant under either tranformation.]

Expanding H' upto second order in x_1 and x_2:

$$\begin{aligned} H' &= \frac{e^2}{R} - \frac{e^2}{R}\left(1 - \frac{x_1}{R} + \frac{x_1^2}{R^2}\right) - \frac{e^2}{R}\left(1 + \frac{x_2}{R} + \frac{x_2^2}{R^2}\right) \\ &\quad + \frac{e^2}{R}\left(1 - \frac{x_1 - x_2}{R} + \frac{x_1^2 + x_2^2 - 2x_1x_2}{R^2}\right) + \mathcal{O}(x^3) \\ &\approx -\frac{2e^2 x_1 x_2}{R^3}. \end{aligned}$$

(b) **(4 points)** Using the change of variables,

$$x_{1,2} = \frac{1}{\sqrt{2}}(x_+ \pm x_-) \qquad \textit{and} \qquad p_{1,2} = \frac{1}{\sqrt{2}}(p_+ \pm p_-),$$

we can rewrite total Hamiltonian H as:

$$\begin{aligned} H &= H^0 + H' \\ H &= \frac{1}{2m}\left(\frac{1}{2}(p_+ + p_-)^2 + \frac{1}{2}(p_+ - p_-)^2\right) + \frac{1}{2k}\left(\frac{1}{2}(x_+ + x_-)^2 + \frac{1}{2}(x_+ - x_-)^2\right) \\ &\quad - \frac{2e^2}{R^3}\frac{1}{2}(x_+ + x_-)(x_+ - x_-) \\ &= \left[\frac{1}{2m}p_+^2 + \frac{1}{2}\left(k - \frac{2e^2}{R^3}\right)x_+^2\right] + \left[\frac{1}{2m}p_-^2 + \frac{1}{2}\left(k + \frac{2e^2}{R^3}\right)x_-^2\right]. \end{aligned}$$

But this is not enough. We further need to show that $[x_\pm, p_\pm] = i\hbar$ and $[x_\pm, p_\mp] = 0$ in order to show that (6.99) is indeed seperated into two independent harmonic oscillator. This is easy but important. [Note: Eq. above differs from Eq. (6.99) in Griffiths by a factor of 2 in the coefficient of e^2/R^3, of course after subtituting $4\pi\epsilon_0 = 1$. So Grfitths has got it wrong everywhere from (6.99) to (6.102). We will independently check it in part (d).]

(c) **(4 points)** Assuming that $k \gg 2e^2/R^3$, we expand $\omega_\pm$ to second order in $2e^2/kR^3$:

$$\begin{aligned} \omega_\pm &= \sqrt{\frac{k \mp 2e^2/R^3}{m}} \\ &= \omega_0\sqrt{1 \mp \frac{2e^2}{kR^3}} \\ &= \omega_0\left[1 \mp \frac{e^2}{kR^3} - \frac{1}{8}\left(\frac{2e^2}{kR^3}\right)^2 + \mathcal{O}\left(\frac{2e^2}{kR^3}\right)^3\right], \end{aligned}$$

where $\omega_0^2 = k/m$. Therefore,

$$\Delta V \equiv E - E_0 \approx -\frac{\hbar}{2m^2\omega_0^3}\frac{e^4}{R^6}.$$

Again this expression differs from (6.102) by a factor of 4 due to same error. But we will see that our answer obtained here is consistent with independent calculation in part (d).

(d) **(6 points)** For our original unperturbed Hamiltonian H^0, we denote eigenstates by $|n_1, n_2\rangle$ and we can write $x_{1,2}$ in terms of creation and annihilation operators $\sqrt{\hbar/2m\omega_0}(a_{1,2} + a_{1,2}^\dagger)$. Hence we obtain,

$$H' = -\frac{\hbar e^2}{m\omega_0 R^3}(a_1 + a_1^\dagger)(a_2 + a_2^\dagger).$$

The first order perturbation to the ground state energy, $\langle 0,0|H'|0,0\rangle = 0$. In order to calculate second order corrections we need to calculate the matrix element $\langle 0,0|H'|n_1,n_2\rangle = -\frac{\hbar e^2}{m\omega_0 R^3}\langle 0,0|(a_1 + a_1^\dagger)(a_2 + a_2^\dagger)|n_1,n_2\rangle$. Since $a_{1,2}^\dagger$ annihilates $\langle 0,0|$, i.e. $\langle 0,0|a_{1,2}^\dagger = 0$, therefore only term contributing to this matrix element will be corresponding to $a_1 a_2$. Hence, noticing that $a|n\rangle = \sqrt{n}\,|n-1\rangle$, we obtain:

$$\begin{aligned}
\langle 0,0|H'|n_1,n_2\rangle &= -\frac{\hbar e^2}{m\omega_0 R^3}\langle 0,0|a_1 a_2|n_1,n_2\rangle \\
&= -\frac{\hbar e^2}{m\omega_0 R^3}\,\sqrt{n_1 n_2}\,\langle 0|n_1 - 1\rangle\langle 0|n_2 - 1\rangle \\
&= -\frac{\hbar e^2}{m\omega_0 R^3}\,\delta_{n_1-1,0}\,\delta_{n_2-1,0}.
\end{aligned}$$

Now second order correction is given by,

$$\begin{aligned}
E_0^{(2)} &= \sum_{n_1,n_2\neq 0}\frac{|\langle 0,0|H'|n_1,n_2\rangle|^2}{-(n_1+n_2)\hbar\omega_0} \\
&= -\frac{\hbar}{2m^2\omega_0^3}\frac{e^4}{R^6},
\end{aligned}$$

which is indeed the same result as what we obtained in part (c).

Note: There is a serious flaw in this problem. If you expand Griffiths' Eq. (6.97) to higher order in $1/R$ you find, in addition to Eq. (6.98), terms that are of order $1/R^4$, $1/R^5$, and so on. All the $1/R^4$ terms and most of the $1/R^5$ terms share in common with the $1/R^3$ term the feature that they do not contribute any first order correction. Their expectation value vanishes in any of the unperturbed states. *However*, among the $1/R^5$ terms, we find in addition a term proportional to

$$\frac{e^2 x_1^2 x_2^2}{R^5}\ ,$$

whose expectation value in the unperturbed ground state is *not* zero. This term in H' therefore leads to a contribution to what Griffiths calls ΔV that is of order $1/R^5$, larger than what Griffiths and you have calculated in Eq. (6.102), and in part (d) by second order perturbation theory using the H' of Eq. (6.98). The bottom line implication of this observation is that Griffiths' ball and spring model is *not* a good model for the real Van der Waals interaction between atoms.