Physics 742 – Graduate Quantum Mechanics 1

Solutions to Chapter 13

6. **[25] In section E we worked out an estimate of the energy between a pair of neutral hydrogen atoms. Consider now the case of a naked proton and a single electron bound to a second proton, as illustrated below.**

(a) [2] Write the Hamiltonian describing the interaction between these three particles. The protons will both be treated as fixed.

There are three interactions, plus the kinetic energy of the electron, so

$$H = \frac{\mathbf{P}^2}{2m} - \frac{k_e e^2}{|\mathbf{R}|} + \frac{k_e e^2}{|\mathbf{a}|} - \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}|}.$$

(b) [2] Divide the Hamiltonian into H_0 and a perturbation W, where the perturbation terms are small in the limit of large a**. How do you describe the quantum states and their energies in the limit of infinite** a**?**

The first two terms are H_0, and the perturbation W is the last two terms.

$$H_0 = \frac{\mathbf{P}^2}{2m} - \frac{k_e e^2}{|\mathbf{R}|} \quad \text{and} \quad W = \frac{k_e e^2}{|\mathbf{a}|} - \frac{k_e e^2}{|\mathbf{a}+\mathbf{R}|}$$

The unperturbed states are $|nlm\rangle$, which have energy $\varepsilon_n = -k_e e^2 / 2n^2 a_0$.

(c) [4] Let $\mathbf{a} = a\hat{\mathbf{z}}$. Expand W to only *linear* order in the displacement R**.**

This is straightforward. As in class, we write

$$\frac{1}{|\mathbf{a}+\mathbf{R}|} = \frac{1}{|a\hat{\mathbf{z}}+\mathbf{R}|} = \left[(a+Z)^2 + X^2 + Y^2\right]^{-\frac{1}{2}} = \frac{1}{a}\left[1 + \frac{2Z}{a} + \frac{\mathbf{R}^2}{a^2}\right]^{-\frac{1}{2}} = \frac{1}{a} - \frac{Z}{a^2}$$

Substituting this into W, we find $W = a^{-2} k_e e^2 Z$.

(d) [5] Find the leading non-vanishing perturbative correction to the ground state energy E_g. The term should have a sum over, say, n, l, and m. What values of l and m contribute?

The linear term in perturbation theory is $\langle 100|W|100\rangle = ke^2 a^{-2}\langle 100|Z|100\rangle = 0$, so we must go to second order in perturbation theory, for which we have

$$E_g = \varepsilon_1 + \sum_{nlm} \frac{\left|\langle nlm|W|100\rangle\right|^2}{\varepsilon_1 - \varepsilon_n} = \varepsilon_1 + \frac{k_e^2 e^4}{a^4} \sum_{nlm} \frac{\left|\langle nlm|Z|100\rangle\right|^2}{\varepsilon_1 - \varepsilon_n}$$

Despite the triple sum, it really isn't as complicated as it seems. In particular, since **R** connects only states with adjacent values of l, we must have $l = 1$. Furthermore, Z commutes with L_z, so we must have $m = 0$. So the expression really is

$$E_g = \varepsilon_1 + \frac{k_e^2 e^4}{a^4} \sum_{n} \frac{\left|\langle n10|Z|100\rangle\right|^2}{\varepsilon_1 - \varepsilon_n}$$

This sum is more complicated than it seems, because in addition to the bound states, we have to include the free states, which we never tried to find the form of.

(e) [7] Find an upper bound on the energy of the ground state at long range by including only the leading term in the sum.

Every term in the sum is negative, so if we include only one term, we end up with an overestimate of the ground state energy. We'll only include $n = 2$, which will yield

$$E_g \le \varepsilon_1 + \frac{k_e^2 e^4}{a^4} \frac{\left|\langle 210|Z|100\rangle\right|^2}{\varepsilon_1 - \varepsilon_2} = \varepsilon_1 + \frac{k_e^2 e^4}{a^4} \frac{\left|\langle 210|Z|100\rangle\right|^2}{-k_e e^2/2a_0 + k_e e^2/8a_0}$$

$$= -\frac{k_e e^2}{2a_0} - \frac{8k_e e^2 a_0}{3a^4}\left|\langle 210|Z|100\rangle\right|^2 = -\frac{k_e e^2}{2a_0} - \frac{8k_e e^2 a_0}{3a^4}\left(\frac{8}{9}\right)^5 a_0^2$$

The final matrix element can be found, for example, in the equation between (13.16) and (13.17), or we can work it out with Maple.

(f) [5] Find a lower bound on the energy of the ground state at long range by including all the terms in the sum, but underestimating the energy denominators.

The smallest denominator occurs when $n = 2$, and hence if we assume $\varepsilon_1 - \varepsilon_n = \varepsilon_1 - \varepsilon_2$ we will *overestimate* the amount the energy is decreased by the perturbation, and hence *underestimate* the energy. Hence we can state with confidence

$$E_g \ge \varepsilon_1 + \frac{k_e^2 e^4}{a^4} \sum_{nlm} \frac{\left|\langle nlm|Z|100\rangle\right|^2}{\varepsilon_1 - \varepsilon_2} = \varepsilon_1 + \frac{k_e^2 e^4}{a^4\left(\varepsilon_1 - \varepsilon_2\right)} \sum_{nlm} \langle 100|Z|nlm\rangle\langle nlm|Z|100\rangle$$

The only term missing in the sum is the unperturbed ground state itself, which doesn't contribute to the sum, so we effectively have a sum over complete states, and we therefore have

$$E_g \ge -\frac{k_e e^2}{2a_0} + \frac{k_e^2 e^4 \langle 100|Z^2|100\rangle}{a^4\left(-k_e e^2/2a_0 + k_e e^2/8a_0\right)} = -\frac{k_e e^2}{2a_0} - \frac{8k_e e^2 a_0 a_0^2}{3a^4}$$

The final matrix element can be found in the equation between (13.20) and (13.21). Comparing the two formulas, we conclude that

$$E_g = -\frac{k_e e^2}{2a_0} - \frac{\gamma k_e e^2 a_0^3}{a^4}$$
$$\tfrac{8}{3}\left(\tfrac{8}{9}\right)^5 < \gamma < \tfrac{8}{3}$$
$$1.480 < \gamma < 2.667$$

Unlike the van der Waals interaction, the potential falls as only the fourth power of distance. I have no idea what the correct value of this parameter is, but I'd guess it's a bit more than 2.