Physics 487 – Homework #6

All solutions must clearly show the steps and/or reasoning you used to arrive at your result. You will lose points for poorly written solutions or incorrect reasoning. Answers given without explanation will not be graded: our master rule for homework and exams is **NO WORK = NO POINTS**. However, unless otherwise specified, you may use any relation from the **formula sheets** on our website, from the introductions to **this or previous homework / discussions**, or from **non-QM courses** without proof. Here's a rule of thumb: Write enough so that it will MAKE SENSE <u>TO YOU</u> IN 5 YEARS, i.e. so that it provides you with useful future notes.

You may also use wolframalpha.com or similar tool to evaluate your integrals
after you set the up in a form that can be **directly entered** into such tools.

Reading for Week 7 : Griffiths Ch. 7 = Variational Principle

Problem 1 : A Second-Order Perturbation Theory Problem   *last problem of Discussion 6*

A particle moves in a 3D SHO with potential energy $V(r)$. A weak perturbation $\delta V(x,y,z)$ is applied:

$$V(r) = \frac{m\omega^2}{2}\left(x^2 + y^2 + z^2\right) \qquad \text{and} \qquad \delta V(x,y,z) = U\,xyz + \frac{U^2}{\hbar\omega}x^2 y^2 z^2$$

where U is a small parameter. Use perturbation theory to calculate the <u>change</u> in the <u>ground state energy</u> to order $O(U^2)$. Use without proof all the results you like from the 1D SHO → see supplementary file Formulae-SHO-reference.pdf on the website.

▶ HINT 1: The energy eigenstates of the 1D SHO™ in our reference file, or in any other sane tabulation, are <u>orthonormal</u>.

▶ HINT 2: Notice that the nth Hermite polynomial, $H_n(x)$, is a polynomial of order n. If you multiply it by x, you turn it into a polynomial of order $n+1$ … which you can write as a linear combination of $H_{n+1}(x)$ and $H_{n-1}(x)$. This relation is *particularly* simple for the ground state. :-)

Problem 2 : The Van der Walls Force — Important for Chemistry!   *adapted from Griffiths 6.31*

Consider two atoms a distance R apart. Because they are electrically neutral you might suppose there would be no force between them, but if they are *polarizable*, there is in fact a weak attraction. To model this system, picture each atom as an electron (mass m, charge $–e$) attached by a spring (spring constant k) to the nucleus
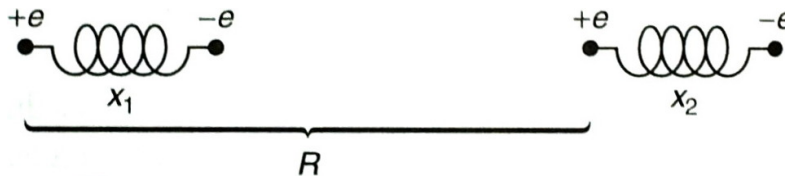
(charge $+e$) as in the figure below :

We'll assume the nuclei are heavy, and essentially motionless. The Hamiltonian for the unperturbed system is

$$H_0 = \frac{1}{2}\frac{p_1^2}{m} + \frac{1}{2}k\,x_1^2 + \frac{1}{2}\frac{p_2^2}{m} + \frac{1}{2}k\,x_2^2$$

The Coulomb interaction between the atoms is

$$H' = \frac{1}{4\pi\varepsilon_0}\left(\frac{e^2}{R} - \frac{e^2}{R-x_1} - \frac{e^2}{R+x_2} + \frac{e^2}{R-x_1+x_2}\right)$$

(a) Explain the form of H' in words. Then, assuming that $|x_1|$ and $|x_2|$ are both much less than R, show that

$$H' \approx -\frac{e^2 x_1 x_2}{2\pi\varepsilon_0 R^3}$$

(b) Using the approximate form of H' from part (a), show that the total Hamiltonian $H = H_0 + H'$ separates in to two harmonic oscillator Hamiltonians :

$$H = \left[\frac{1}{2m}p_+^2 + \frac{1}{2}\left(k - \frac{e^2}{2\pi\varepsilon_0 R^3}\right)x_+^2\right] + \left[\frac{1}{2m}p_-^2 + \frac{1}{2}\left(k + \frac{e^2}{2\pi\varepsilon_0 R^3}\right)x_-^2\right]$$

under the change of variables

$$x_\pm = \frac{1}{\sqrt{2}}(x_1 \pm x_2), \text{ which implies } p_\pm = \frac{1}{\sqrt{2}}(p_1 \pm p_2).$$

(c) The ground state energy for this Hamiltonian is evidently

$$E = \frac{1}{2}\hbar(\omega_+ + \omega_-), \text{ where } \omega_\pm = \sqrt{\frac{k \mp (e^2/2\pi\varepsilon_0 R^3)}{m}}.$$

Without the Coulomb interaction, it would have been $E_0 = \hbar\omega_0$, where $\omega_0 = \sqrt{k/m}$.
Assuming that $k \gg (e^2/2\pi\varepsilon_0 R^3)$, show that

$$\Delta V \equiv E - E_0 \approx -\frac{\hbar}{8m^2\omega_0^3}\left(\frac{e^2}{2\pi\varepsilon_0}\right)^2 \frac{1}{R^6}.$$

Conclusion: There is an **attractive potential** between the atoms, proportional to the <u>inverse sixth power</u> of their separation.. This is the **van der Waals interaction** between two neutral atoms.

(d) Now do the same calculation by applying second-order perturbation theory to the original H_0 from the introduction and the approximate H' from part (a). Hint: The unperturbed states are of the form $\psi_{n1}(x_1)\,\psi_{n2}(x_2)$, where $\psi_n(x)$ is a one-particle oscillator wave function with mass m and spring constant k; ΔV is the second-order correction to the ground state energy, for the perturbation H' in part (a) (notice that the *first*-order correction is zero.)

▶ HINT: Remember that the eigenstates of energy of the 1D SHO™ (as tabulated on one of our formula sheets for your convenience) are all <u>orthonormal</u>. The integral(s) you have to do can be performed using this fact : The nth Hermite polynomial, $H_n(x)$, is a polynomial of order n. If you multiply it by x, you turn it into a polynomial of order $n+1$ ... which you can write as a linear combination of $H_{n+1}(x)$ and $H_{n-1}(x)$. :-)

Problem 3 : The Stark Effect   *Griffiths 6.36*

When an atom is placed in a uniform external electric field E_{ext}, the energy levels are shifted — a phenomenon known as the **Stark effect**. In this problem we analyze the Stark effect for the $n = 1$ and $n = 2$ states of hydrogen. Let the field point in the z direction, so the potential energy of the electron is

$$H'_S = e\,E_{\text{ext}}\,z = e\,E_{\text{ext}}\,r\cos\theta$$

Treat this as a perturbation on the simple "Bohr" Hamiltonian for the hydrogen atom,

$$H_0 = -\frac{\hbar^2\nabla^2}{2m} - \frac{e^2}{4\pi\varepsilon_0\,r}\ .$$

Spin is irrelevant to this problem so ignore it.

(a) Show that the ground state energy is not affected by this perturbation, to first order.

(b) The first excited state is 4-fold degenerate: ψ_{200}, ψ_{211}, ψ_{210}, ψ_{21-1}. Using degenerate perturbation theory, determine the first-order corrections to the energy. Into how many levels does E_2 split?

(c) What are the "β" wave functions for part (b), i.e. the ones that diagonalize the perturbation H'_S? (Griffiths calls these "good" wavefunctions.) Find the expectation value of the electric dipole moment ($\vec{p}_e = -e\vec{r}$) in each of these "good" states. Notice that the results are independent of the applied field — evidently hydrogen in its first excited state can carry a *permanent* electric dipole moment.

▶ **HINT**: There are a lot of integrals in this problem, but almost all of them are ZERO. So study each one carefully before you do any calculations! For example, if the ϕ integral vanishes, there's not much point in doing the r and θ integrals ☺. Partial answer: $H'_{13} = H'_{31} = -3\,e\,a_0\,E_{\text{ext}}$ where a_0 is the Bohr radius as usual; all other elements of $\mathbf{H}'_{ij} \equiv \left\langle \beta_i^{(0)} \middle| H' \middle| \beta_j^{(0)} \right\rangle$ are zero ☺.