Homework #6 — Phys623 — Spring 1999
Deadline: 5 p.m., Friday, March 19, 1999.
Turn in homework in the class or put in the box on the door of Phys 2314 by 5 p.m.

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Do not forget to write your name and the homework number!
Equation numbers with the period, like (3.25), refer to the equations of Schwabl.
Equation numbers without period, like (5), refer to the equations of this homework.

Helium (Chapter 13.2)

1. [**5 points**] Schwabl's Problem 13.1.

2. *Qualifier, January 1999, II-2.*

   Two particles, each of mass m, are confined in one dimension to a box of length L.

   (a) [**1 points**] First consider the case where the particles are spinless, not identical, and do not interact between themselves.

   What are the normalized two-particle wave functions and energies of the three lowest-energy states of the system? Are any of these energy levels degenerate?

   (b) [**3 points**] Suppose the particles interact between themselves with the potential $V = \lambda\delta(x_1 - x_2)$, where x_1 and x_2 are the coordinates of the particles, $\delta(x)$ is the one-dimensional Dirac delta-function, and $\lambda > 0$.

   In the lowest order of perturbation theory in V calculate the energies and two-particle wave functions for the three lowest-energy states of the system. Sketch how the energy levels shift relative to the energy levels of the noninteracting system.

   (c) [**2 points**] Formulate a condition on the coefficient λ for lowest order perturbation theory to be applicable.

   (d) [**3 points**] Now suppose that the particles are two identical fermions, each of spin 1/2, interacting via the potential V of part 2b. Explain how the Pauli principle determines the values of the total spin of the system for the three energy levels found in part 2b. Write the values of the total spin and the degeneracy next to the energy levels in the diagram of part 2b.

   (e) [**2 points**] Let us interpret the studied model as a crude, qualitative model of the helium atom, with the potential box standing in for the attractive potential of the nucleus, the lowest energy states corresponding to the 1s and 2s states, and the potential V standing in for the Coulomb repulsion between the electrons.

   On the basis of your results, qualitatively explain the structure and the quantum numbers of the three lowest-energy states of the helium atom.

   Possibly useful integrals:

$$\int_0^\pi d\phi \, \sin^4\phi = 3\pi/8 \qquad \int_0^\pi d\phi \, \sin^2\phi \, \sin^2 2\phi = \pi/4$$

3. *Adapted from Qualifier, January 1993, II-4.*

   Consider a Li^+ ion: an atom with 2 electrons and the nuclear charge $Z = 3$.

   (a) [**3 points**] In the spirit of Sections 13.2.1–13.2.2, write down the electronic wave functions for the lowest and the first excited energy levels of this ion in terms of the hydrogen one-electron wave functions. What are the degeneracy, the orbital angular momentum L and the total spin S of each state?

(b) [**3 points**] In the first-order perturbation theory, the ground-state energy of the He atom is –5.5 Ry (Eq. (13.27a)). In the same approximation, find the ground-state energy of the Li^+ ion. You don't need to repeat the whole derivation from the textbook; just rescale the answers using $Z = 3$ instead of $Z = 2$.

(c) [**3 points**] Following Section 13.2.3, find the ground-state energy of the Li^+ ion using the variational method. Compare result with that of Problem 3b.

(d) [**5 points**] Suppose one of the electrons is replaced by a muon, an electron-like particle with a much heavier mass $m_\mu = 207\, m_e$. Developing a sensible picture of the Coulomb charge screening for this atom, find the wave functions and the energies of the lowest and the first excited energy levels.

The Thomas-Fermi Method (Chapter 13.4)

4. *Adapted from Physics Qualifier, May 1969, Problem II-1.*

(a) Show that a scale transformation:

$$\mathbf{r} \to \lambda \mathbf{r}, \qquad \mathbf{p} \to \mathbf{p}/\lambda, \tag{1}$$

(where $\mathbf{r}$ and $\mathbf{p}$ are the coordinate and momentum operators, and λ is a constant) can be realized in quantum mechanics as a unitary transformation by each of the following two methods:

i. [**3 points**] Let $\psi(\mathbf{r})$ be a normalized wave function satisfying the Schrödinger equation. Explicitly write the Schrödinger equation in the scale-transformed coordinates and show that there is a normalized wave function $\psi_\lambda(\mathbf{r})$ that satisfies the scale-transformed Schrödinger equation. Express explicitly $\psi_\lambda(\mathbf{r})$ in terms of $\psi(\mathbf{r})$.

ii. [**7 points**] Consider the unitary operator:

$$\hat{R}(\lambda) = \exp\left\{-\frac{i \ln \lambda}{2\hbar}(\mathbf{pr} + \mathbf{rp})\right\}. \tag{2}$$

Show that **(see Hints)**

$$\hat{R}^+(\lambda)\mathbf{r}\hat{R}(\lambda) = \lambda \mathbf{r}, \qquad \hat{R}^+(\lambda)\mathbf{p}\hat{R}(\lambda) = \mathbf{p}/\lambda. \tag{3}$$

What is the result of applying $\hat{R}(\lambda)$ to $\psi(\mathbf{r})$: $\hat{R}(\lambda)\psi(\mathbf{r})$?

(b) [**5 points**] Suppose now that a particle interacts with a potential described by a homogeneous function of the order ν, such that for any constant λ

$$V(\lambda \mathbf{r}) = \lambda^\nu V(\mathbf{r}). \tag{4}$$

(For harmonic oscillator $\nu = 2$, for Coulomb potential $\nu = -1$.)

Let $|E\rangle$ be an eigenstate of the Hamiltonian with the eigenvalue E and let $|\lambda, E\rangle = \hat{R}(\lambda)|E\rangle$ be the scale-transformed state. The expectation value of the Hamiltonian should not depend on the representation used:

$$E = \langle E|\hat{H}|E\rangle = \langle E|\hat{R}^+(\lambda)\hat{R}(\lambda)\hat{H}\hat{R}^+(\lambda)\hat{R}(\lambda)|E\rangle = \langle \lambda, E|\hat{H}_\lambda|\lambda, E\rangle, \tag{5}$$

where $\hat{H}_\lambda = \hat{R}(\lambda)\hat{H}\hat{R}^+(\lambda)$ is the scale-transformed Hamiltonian.

From Eq. (5), derive a relation between the average kinetic, $\langle T\rangle$, and potential, $\langle V\rangle$, energies in an energy eigenstate $|E\rangle$ (the virial theorem) **(see Hints)**:

$$\nu\langle V\rangle = 2\langle T\rangle. \tag{6}$$

[The virial theorem is also proved in a different way on page 218 of Schwabl (see Eqs. (12.24) and (12.25)).]

5. *Adapted from Qualifier, Fall 1981, II-1.*

The Thomas-Fermi model of an atom can be also developed using the variational principle. Suppose electrons have an arbitrary, spherically-symmetrical density $n(r)$. The energy of the electrons can be expressed as a functional of the electron density, $E\{n(r)\}$. The actual electron density in the atom, $n_0(r)$, is determined as the density that minimizes the energy functional $E\{n(r)\}$.

(a) [**5 points**] Write down the energy functional $E\{n(r)\}$ for a neutral atom with the nuclear charge Ze. The functional $E\{n(r)\}$ should contain three terms:

i. E_{ne} that describes the Coulomb interaction between the electrons and the nucleus, which is treated as a point charge Ze;

ii. E_{ee} that describes the Coulomb interaction between the electrons;

iii. T that describes the kinetic energy of the electrons. This term is written in the quasi-classical approximation, assuming that the electron density $n(r)$ at a given point $\mathbf{r}$ defines a local Fermi energy $E_F(r)$, which determines the kinetic energy of the electrons at the given point (see Eq. (13.61)). The total kinetic energy is the integral of the local kinetic energy over the whole space $\mathbf{r}$.

(b) i. [**5 points**] By varying $n(r)$ in $E\{n(r)\}$, find an integral equation for $n_0(r)$. Take into account that we are looking for a minimum of energy with a given total number of electrons $\int n(r)\, d^3r = Z$, thus it is necessary to introduce a Lagrange multiplier in the variational procedure. Identify various terms in the obtained equation as the electrostatic Hartree potential $V(r)$ given by Eq. (13.58) and the chemical potential μ denoted as ε_F in Chapter 13.4. Show that the obtained equation is equivalent to Eq. (13.60) squared.

ii. [**5 points**] By applying the Laplace operator Δ to the equation obtained in Problem 5(b)i, find a differential equation for $n_0(r)$. Show that this equation is equivalent to Eq. (13.63)

(c) [**7 points**] Using the variational principle, but without explicitly finding the optimal density $n_0(r)$, find the ratios E_{ne}/E_{ee} and $(E_{ne} + E_{ee})/T$ in the Thomas-Fermi atom (that is, when $n(r) = n_0(r)$ in E_{ne}, E_{ee} and T) **(see Hints)**. Check whether the latter ratio is in agreement with the virial theorem.

(d) i. [**2 points**] Does a neutral Thomas-Fermi atom have a well-defined radius R where $n_0(R) = 0$, or does $n_0(r)$ extend to infinity? What about a positively charged Thomas-Fermi ion? Can the Thomas-Fermi method describe a negatively charged ion?

ii. [**2 points**] How does the average distance between the electrons and the nucleus depend on the nucleus charge Z? (That is, to which power of Z is it proportional?)

iii. [**2 points**] How does the total ionization energy of the atom (the energy necessary to remove all Z electrons from the atom) depend on Z? (To which power of Z is it proportional?)

(e) [**7 points**] In a neutral Thomas-Fermi atom, how does the number of electrons in the s-state depend on the nuclear charge Z? (To which power of Z is it proportional?) **(see Hints)**

Atomic Structure and Hund's Rules (Chapter 13.5)

6. [**5 points**] Schwabl's Problem 13.3.

7. [**3 points**] Schwabl's Problem 13.4.

Hints

4(a)ii The following operator identity may be helpful:

$$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \hat{B} + [\hat{A},\hat{B}] + \frac{1}{2!}[\hat{A},[\hat{A},\hat{B}]] + \ldots. \tag{7}$$

4b Differentiate (5) by λ, set λ to 1, and take into account that

$$\frac{d}{d\lambda}\langle\lambda, E|\lambda, E\rangle = 0, \tag{8}$$

because $\langle\lambda, E|\lambda, E\rangle = 1$.

5c Consider the variations of the functional $E\{n(r)\}$ under the following variations of the density: $n(r) = (1+\lambda)n_0(r)$ and $n(r) = n_0[(1+\lambda)r]$ with an infinitesimal λ. The variations of the functional must equal zero, because these are the variations near the optimal configuration $n_0(r)$.

5e In order to determine the number of electrons in the s-state, use the Bohr-Sommerfeld quantization condition for the radial motion of the electrons with the angular momentum $l = 0$ in Thomas-Fermi-Hartree potential $V(r)$. Use the similarity law for $V(r)$ at different Z to determine how this expression depends on Z.