

PROBLEM SET #2 SOLUTIONS

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PROBLEM 1

a). On the scale of atomic units, the electron of mass m_e is confined to a region of size a_0 . From quantum mechanics, this confinement imparts the electron kinetic energy on the order of:

$$T \sim \frac{\hbar^2}{m_e} \left(\frac{1}{a_0} \right)^2 = \frac{\hbar^2}{m_e a_0^2}$$

Balancing this confinement energy against the electrostatic attraction to the proton gives:

$$\frac{\hbar^2}{m a_0^2} = \frac{e^2}{a_0} \Rightarrow a_0 = \frac{\hbar^2}{m e^2}$$

Coincidentally, this is the exact expression for the Bohr radius (the atomic unit of length).

b). Classically, the nucleus sees the orbiting electron as a current loop C with radius a_0 , carrying current $I = e/T$ where $T = 2\pi a_0/v$ is the period of the electron's orbit. In cgs units, at its center, this loop produces magnetic field given by Ampere's law:

$$B_N = \frac{I}{c} \int_C \frac{dl \times r}{r^3} = \frac{I}{c} \frac{2\pi a_0^2}{a_0^3} = \frac{2\pi I}{c a_0} = \frac{e}{c a_0^2} v$$

The electron's velocity can be found from the momentum p produced by its confinement as

$$v = p/m = m^{-1} \hbar / a_0 = m^{-1} \hbar / (\hbar^2 / e^2) = e^2 / \hbar = \alpha c$$

where α is the fine structure constant.

The same result can be obtained from quantization of electron's angular momentum:

$$m v a_0 \approx \hbar \Rightarrow v = \hbar / (a_0 m) = \alpha c$$

Finally:

$$B_N = \frac{e}{a_0^2} \alpha = \frac{m_e^2 e^7}{\hbar^5 c}$$

c). In cgs units, a Bohr magneton is

$$\mu_B = \frac{e\hbar}{2m_e c} = \frac{e\hbar}{2(\hbar^2/(a_0 e^2))c} = \frac{e^3 a_0}{2\hbar c} = \frac{\alpha e a_0}{2}$$

while a Hartree can be expressed as $H_0 = m_e c^2 \alpha^2 = e^2/a_0$. Then:

$$B_H = H_0/\mu_B = \frac{e^2}{a_0} \frac{2}{\alpha e a_0} = \frac{2}{\alpha} \frac{e}{a_0^2} = \frac{2m_e^2 e^3 c}{\hbar^3}$$

d). >From part b),

$$B_N = \frac{e}{a_0^2} \alpha = E_A \alpha$$

while from part c)

$$B_H = \frac{2}{\alpha} \frac{e}{a_0^2} = 2E_A/\alpha$$

e). B_N corresponds to the magnetic field produced by the orbiting electron in a hydrogen atom and as such gives the typical scale of magnetic fields due to motion of atomic charges. This makes it the preferred choice for an atomic unit of magnetic field.

Since the hydrogen electron moves at velocity α^{-1} smaller than the speed of light, the magnetic field B_N that it produces is α^{-1} times smaller than its electric field E_A . In SI units:

$$B_N = \frac{e}{4\pi\epsilon_0} \frac{\alpha}{a_0} \frac{1}{c} = 12.52T$$

At this practically accessible field, the Zeeman interaction with the external field becomes comparable to even the strongest magnetic coupling in atoms ($L.S$ coupling).

A Bohr magneton corresponds to the magnetic moment of the hydrogen electron's orbital motion. Therefore, B_H corresponds to the magnetic field which interacts with this electron on the same energy scale as the nuclear electric field. Since the hydrogen electron moves α^{-1} times slower than the speed of light, B_H is α^{-1} larger than E_A and α^{-2} i.e. 5 orders of magnitude larger than both the atomic and the highest laboratory magnetic fields.

PROBLEM 2

a). In cgs units, the Rydberg constant is given by:

$$R_\infty = \frac{m_e e^4}{4\pi c \hbar^3}$$

while

$$\alpha = \frac{e^2}{\hbar c}$$

Hence:

$$f_\infty/\alpha^2 = cR_\infty/\alpha^2 = \frac{cm_e e^4 \hbar^2 c^2}{4\pi c \hbar^3 e^4} = \frac{m_e c^2}{4\pi \hbar} = \frac{m_e c^2/h}{2} = \frac{f_e}{2}$$

In SI units:

$$R_\infty = \frac{m_e e^4}{8c\epsilon_0^2 \hbar^3}$$

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{e^2}{2\epsilon_0 \hbar c}$$

so also:

$$f_\infty/\alpha^2 = \frac{m_e e^4}{8\epsilon_0^2 \hbar^3} \frac{4\epsilon_0^2 \hbar^2 c^2}{e^4} = \frac{m_e c^2}{2\hbar} = \frac{f_e}{2}$$

where f_e is the electron's 'rest frequency'. In other words,

$$\alpha = \sqrt{\frac{2f_\infty}{f_e}} = \sqrt{\frac{2f_\infty}{m_e c^2/h}} = \sqrt{2R_\infty \frac{h}{m_e c}}$$

In SI units, by the definition of the meter, the speed of light is fixed at $c = 299,792,458 \text{ m/s}$. Hence, α depends only on the experimental values of R_∞ and h/m_e .

b). Typically, this experiment would be done with a non-relativistic (thermal) neutron beam as its deBroglie wavelength would be much larger and more easily measurable. The momentum of such a non-relativistic neutron is related by its de Broglie wavelength as $\lambda_B = h/p$. Since $p = mv$, we get $h/m = \lambda_B v$.

c). The photon of frequency ν carries momentum $p_\gamma = h\nu/c$. In the absorption process the momentum is conserved so

$$mv_R(\nu) = h\nu/c$$

or

$$h/m = cv_R(\nu) / \nu$$

d). When the atom absorbs the first photon, it is imparted a recoil velocity given by the expression from part c):

$$v_R^a = v_R(\nu_1) \approx \frac{h\nu_1}{cm}$$

When the atom emits the photon, it emits it into a beam propagating opposite of its direction of motion. This emission is accompanied by another recoil, in the same direction as the first, corresponding to the frequency ν_2 :

$$v_R^b = v_R(\nu_2) \approx \frac{h\nu_2}{cm}$$

Since the atomic light-recoil velocities are much smaller than the speed of light, their effect on the atomic resonance will be small and $\nu_1 \approx \nu_2 \approx \nu_0$. Then, by the total conservation of energy:

$$0 + h\nu_1 = h\nu_2 + \frac{m}{2} (v_R^a + v_R^b)^2$$

i.e.

$$h(\nu_1 - \nu_2) \approx \frac{m}{2} \left(\frac{h}{cm} \right)^2 (\nu_1 + \nu_2)^2$$

$$\frac{\nu_1 - \nu_2}{(\nu_1 + \nu_2)^2} \approx \frac{h}{2mc^2}$$

i.e.

$$\frac{1}{2} \frac{\Delta\nu c^2}{\nu_0^2} \approx \frac{h}{m}$$

Note the factor of 1/2 which appears due to the second atomic recoil accompanying the emission of the photon (see PRL **70**, 18, 2706 (1993)).

e). The relationship between $h/\Delta m$ and λ will depend somewhat on the effect of the recoil of the nucleus. If we neglect the recoil, by mass-energy equivalence we get directly

$$\Delta mc^2 = h\nu = \frac{hc}{\lambda}$$

and

$$\frac{h}{\Delta m} = \lambda c$$

Since c in SI units is a constant, this only depends on the experimental value of λ in meters.

Since this is a precision measurement, let's try to consider the effect of non-relativistic nuclear recoil. By mass-energy equivalence and Newtonian momentum conservation:

$$\Delta mc^2 = \frac{hc}{\lambda} + \frac{(m - \Delta m) v^2}{2}$$

$$\frac{h}{\lambda} = (m - \Delta m) v$$

Solving for λ :

$$\frac{h}{\lambda} = c \left(\Delta m - m + \sqrt{m^2 - \Delta m^2} \right)$$

$$\lambda \approx \frac{h}{c\Delta m} \left(1 + \frac{\Delta m}{2m} + O \left(\frac{\Delta m}{m} \right)^2 \right)$$

The next-order contribution from the recoil correction scales as $\Delta m/m$. For the 2.2MeV γ -ray transition in deuterium (Nature, **438**, 1096-1097), the above recoil correction is on the order of 1.2×10^{-3} – well inside the accuracy of mass balances. Unfortunately, this correction is off by a factor of two as can be verified by a full relativistic treatment:

$$\frac{hc}{\lambda} + \frac{m'c^2}{1 - \frac{v^2}{c^2}} = mc^2$$

$$\frac{m'v}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{h}{\lambda}$$

\Rightarrow :

$$\lambda = \frac{h}{c\Delta m} \frac{1}{2} \left(1 + \sqrt{\frac{1+3\delta}{1-\delta}} \right) \approx \frac{h}{c\Delta m} (1 + \delta + \delta^3 - \delta^4 + 3\delta^5 + O(\delta^6)), \delta = \frac{\Delta m}{m}$$

$$\lambda \approx \frac{h}{c\Delta m} \left(1 + \frac{\Delta m}{m} + \dots \right)$$

This means that the first recoil correction for the emission of a 2.2MeV γ -ray from 2H is on the order of 3×10^{-3} .

PROBLEM 3

a). If we assume the spin wavefunction to be antisymmetric, the spatial electronic wavefunction will be symmetric. If both electrons are in the 1S state, we get

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1S}(\mathbf{r}_1) \psi_{1S}(\mathbf{r}_2)$$

The electron-electron interaction energy $\left\langle \frac{e^2}{r_{12}} \right\rangle$ can then be written as:

$$\begin{aligned} V_{ee} = \left\langle \frac{e^2}{r_{12}} \right\rangle &= \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 |\psi_{1S}(\mathbf{r}_1)|^2 |\psi_{1S}(\mathbf{r}_2)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= \int d^3\mathbf{r}_1 |\psi_{1S}(\mathbf{r}_1)|^2 eU(\mathbf{r}_1) \\ &= \langle \psi_{1S}(r_1) | eU(r_1) | \psi_{1S}(r_1) \rangle \end{aligned}$$

where

$$U(\mathbf{r}_1) = \int d^3\mathbf{r}_2 |\psi_{1S}(\mathbf{r}_2)|^2 \frac{e}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

can be thought of as average electrostatic potential produced by the second electron's effective charge distribution $\rho(\mathbf{r}_2) = e |\psi_{1S}(\mathbf{r}_2)|^2$.

If both electrons are in S orbitals, $\rho(\mathbf{r}_2)$ will be spherically symmetric. Then, $U(\mathbf{r}_1)$ can be obtained simply by adding up the contributions due to each spherical shell with charge $dq = e |\psi_{1S}(r_2)|^2 4\pi r_2^2 dr_2$:

$$U(r_1) = \int_{r_2 < r_1} \frac{dq}{r_1} + \int_{r_2 > r_1} \frac{dq}{r_2}$$

Substituting the hydrogenic ground state wavefunction:

$$\psi_{1S}(r) = \frac{1}{a^{3/2}\sqrt{\pi}} e^{-r/a}, \quad a = a_0/Z$$

$$\begin{aligned}
 dq &= \frac{e}{\pi a^3} e^{-2r_2/a} 4\pi r_2^2 dr_2 \\
 U(r_1) &= \frac{e}{\pi a^3} \left\{ \int_{r_2 < r_1} \frac{1}{r_1} e^{-2r_2/a} 4\pi r_2^2 dr_2 + \int_{r_2 > r_1} \frac{1}{r_2} e^{-2r_2/a} 4\pi r_2^2 dr_2 \right\} \\
 &= \frac{4e}{a} \left\{ \frac{1}{r_1/a} \int_{x < r_1/a} e^{-2x} x^2 dx + \int_{x > r_1/a} \frac{1}{x} e^{-2x} x^2 dx \right\} \\
 &= \frac{e}{r_1} \left(1 - e^{-2r_1/a} (1 + r_1/a) \right)
 \end{aligned}$$

Therefore:

$$\begin{aligned}
 V_{ee} &= \frac{e}{\pi a^3} \int_0^\infty \frac{e}{r_1} \left(1 - e^{-2r_1/a} (1 + r_1/a) \right) e^{-2r_1/a} 4\pi r_1^2 dr_1 \\
 &= \frac{e^2}{a} \int_0^\infty \frac{1}{x} (1 - e^{-2x} (1 + x)) e^{-2x} 4x^2 dx \\
 &= \frac{e^2}{a} \int_0^\infty (e^{-2x} - e^{-4x} (1 + x)) 4x dx \\
 &= \frac{5}{8} \frac{e^2}{a} = \frac{5Z}{8} \frac{e^2}{a_0} = 34.014 eV
 \end{aligned}$$

Therefore, the first variational estimate for the ground state energy is:

$$E = \left(-Z^2 + \frac{5Z}{8} \right) \frac{e^2}{a_0} = -74.831 eV$$

Part b). In He, the nucleus is $\sim 4000X$ heavier than each electron. Therefore, we neglect nuclear motion, and rewrite the He Hamiltonian as:

$$H = H_1 + H_2 + \frac{(Z' - 2)}{r_1} e^2 + \frac{(Z' - 2)}{r_2} e^2 + \frac{e^2}{r_{12}}$$

where

$$H_{1,2} = \left(\frac{p_{1,2}^2}{2m_e} - \frac{Z' e^2}{r_{1,2}} \right)$$

correspond to hydrogenic Hamiltonians with reduced mass m_e , charge Z' and ground state eigenfunction $\phi(\vec{r})$ with eigenvalue $E_1 = -e^2/2a = -e^2 Z'^2 / 2a_0$. From class, $\langle \phi | r^{-1} | \phi \rangle = a^{-1} = Z' / a_0$.

Finally, from part a),

$$\langle \phi(r_1) \phi(r_2) | \frac{e^2}{r_{12}} | \phi(r_1) \phi(r_2) \rangle = \frac{5Z'}{8} \frac{e^2}{a_0}$$

Therefore,

$$\begin{aligned} E_0(Z') = \langle \phi(r_1)\phi(r_2) | H | \phi(r_1)\phi(r_2) \rangle &= 2E_1 + \frac{e^2}{a_0} \left\{ 2(Z' - 2)Z' + \frac{5Z'}{8} \right\} \\ &= \frac{e^2}{a_0} \left\{ Z'^2 - 4Z' + \frac{5Z'}{8} \right\} \\ &= \frac{e^2}{a_0} \left\{ Z'^2 - \frac{27}{8}Z' \right\} \end{aligned}$$

Z' is the effective nuclear charge as seen by each electron. The bare nuclear charge is reduced below $Z = 2$ due to the screening effect of the other electron.

Part c). Setting $\partial_{Z'} E_0 = 0$, $2Z' - 27/8 = 0$ or $Z' = 27/16 = 1.6875$. In other words, due to shielding, each electron sees only 84% of the nuclear charge. At this optimal Z' value we get the new best variational estimate of ground state energy:

$$E_0 = - \left(\frac{27}{16} \right)^2 \frac{e^2}{a_0} = -77.489 \text{ eV}$$