Problem Set #3 Solutions

Yu-Kun Lu

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Problem 1

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:

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

In SI units:

$$\begin{aligned} R_\infty &= \frac{m_e e^4}{8c\epsilon_0^2 h^3} \\ \alpha &= \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{e^2}{2\epsilon_0 hc} \end{aligned}$$

so also:

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

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 $c = 299,792,458\, m/s$. 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:

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

i.e.

$$
\begin{aligned}
h\left(\nu_1-\nu_2\right) &\approx \frac{m}{2}\left(\frac{h}{cm}\right)^2\left(\nu_1+\nu_2\right)^2 \\
\frac{\nu_1-\nu_2}{\left(\nu_1+\nu_2\right)^2} &\approx \frac{h}{2mc^2}
\end{aligned}
$$

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 nonrelativistic nuclear recoil. By mass-energy equivalence and Newtonian momentum conservation:

$$
\begin{aligned}
\Delta mc^2 &= \frac{hc}{\lambda} + \frac{(m-\Delta m)\, v^2}{2} \\
\frac{h}{\lambda} &= (m-\Delta m)\, v
\end{aligned}
$$

Solving for λ:

$$
\begin{aligned}
\frac{h}{\lambda} &= c\left(\Delta m - m + \sqrt{m^2-\Delta m^2}\right) \\
\lambda &\approx \frac{h}{c\Delta m}\left(1+\frac{\Delta m}{2m}+O\left(\frac{\Delta m}{m}\right)^2\right)
\end{aligned}
$$

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:

$$
\begin{aligned}
\frac{hc}{\lambda}+\frac{m'c^2}{1-\frac{v^2}{c^2}} &= mc^2 \\
\frac{m'v}{\sqrt{1-\frac{v^2}{c^2}}} &= \frac{h}{\lambda}
\end{aligned}
$$

$\Rightarrow$:

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

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 2

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

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

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

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

where

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

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

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 $dq = e\left|\psi_{1S}(r_2)\right|^2 4\pi r_2^2 dr_2$:

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

Substituting the hydrogenic ground state wavefunction:

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

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

Therefore:

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

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

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

b)

In He, the nucleus is ∼4000X heaver 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 $E_1 = -e^2/2a = -e^2Z'^2/2a_0$. 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.

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:

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

Problem 3

Note on grading: this question is out of 3. Part a) has 0.5 point, b) 1.5 point, and c) 1 point.

a)

Since the charge density is everywhere finite, the field $\vec{E}$ is continuous, while the spherical symmetry of the problem gives $\vec{E} = E_r\hat{r}$. Invoking Gauss' law $\oint \vec{E}\cdot d\vec{S} = 4\pi Q_{\text{enc}}$ (cgs units) for a spherical surface of radius r around the origin gives:

$$4\pi r^2 E_r = 4\pi \begin{cases} \frac{4}{3}\pi r^3\rho_0 & (r < a) \\ \frac{4}{3}\pi a^3\rho_0 & (r > a) \end{cases}$$

$$E_r = \frac{4}{3}\pi a\rho_0 \begin{cases} \frac{r}{a} & (r < a) \\ \frac{a^2}{r^2} & (r > a) \end{cases}$$

Then,

$$\boxed{\phi(r) = -\int_\infty^r E_{r'}dr' = \frac{4}{3}\pi a^2\rho_0 \begin{cases} \frac{1}{2}\left(3 - \left(\frac{r}{a}\right)^2\right) & (r < a) \\ \frac{a}{r} & (r > a) \end{cases}}$$

b)

The total charge of the proton is e, so that

$$\rho_0 = \frac{e}{\frac{4}{3}\pi a^3}$$

The potential for the electron is thus

$$U = -e\phi = -\frac{e^2}{a} \begin{cases} \frac{1}{2}\left(3 - \left(\frac{r}{a}\right)^2\right) & (r < a) \\ \frac{a}{r} & (r > a) \end{cases}$$

The effect of the finite size of the proton is the deviation of the potential from the point source case, $U = -e^2/r$.

$$\Delta U = \begin{cases} -\frac{e^2}{2a}\left(3 - \left(\frac{r}{a}\right)^2 - \frac{2a}{r}\right) & (r < a) \\ 0 & (r > a) \end{cases}$$

Working in first order perturbation theory, the energy shift of the $1S$ state, ΔU_{1S}, is given as

$$\Delta U_{1S} = \langle\psi_{1S}|\,\Delta U\,|\psi_{1S}\rangle = \int \Delta U|\psi_{1S}(\vec{r})|^2 d\vec{r}$$

Since the proton radius a is very much less than the Bohr radius a_0, $\psi_{1S}(\vec{r}) \sim \psi_{1S}(0)$ in the region where ΔU is non-zero.

$$\Delta U_{1S} = \frac{1}{\pi a_0^3}\int_{r<a} \Delta U d\vec{r} = \frac{4}{5}\frac{e^2}{2a_0}\left(\frac{a}{a_0}\right)^2$$

$$= \frac{4}{5}13.606\text{ eV}\left(\frac{0.9\text{ fm}}{53\text{ pm}}\right)^2 = 3.14\times 10^{-9}\text{ eV} = \boxed{759\text{ kHz}}$$

c)

Since the probability density at the origin scales as n^{-3}, $\Delta U_{2S} = \Delta U_{1S}/8$ and the shift of the $1S - 2S$ transition frequency is

$$\Delta U_{1S-2S} = \left(1 - \frac{1}{8}\right) \Delta U_{1S} = 664 \text{ kHz}$$

Since $\Delta U_{1S-2S} \propto a^2$,

$$\frac{\delta\left(\Delta U_{1S-2S}\right)}{\Delta U_{1S-2S}} = 2\frac{\delta a}{a}$$

$$\delta\left(\Delta U_{1S-2S}\right) \sim 2\frac{0.01}{0.9} 664 \text{ kHz} = \boxed{15 \text{ kHz}}$$

The frequency of the $1S - 2S$ transition is

$$3/4 \times 13.606 \text{ eV} = 10.2 \text{ eV} = 2.5 \times 10^{15} \text{ Hz}$$

Therefore, this requires $\boxed{6 \times 10^{-12}}$ relative frequency accuracy.