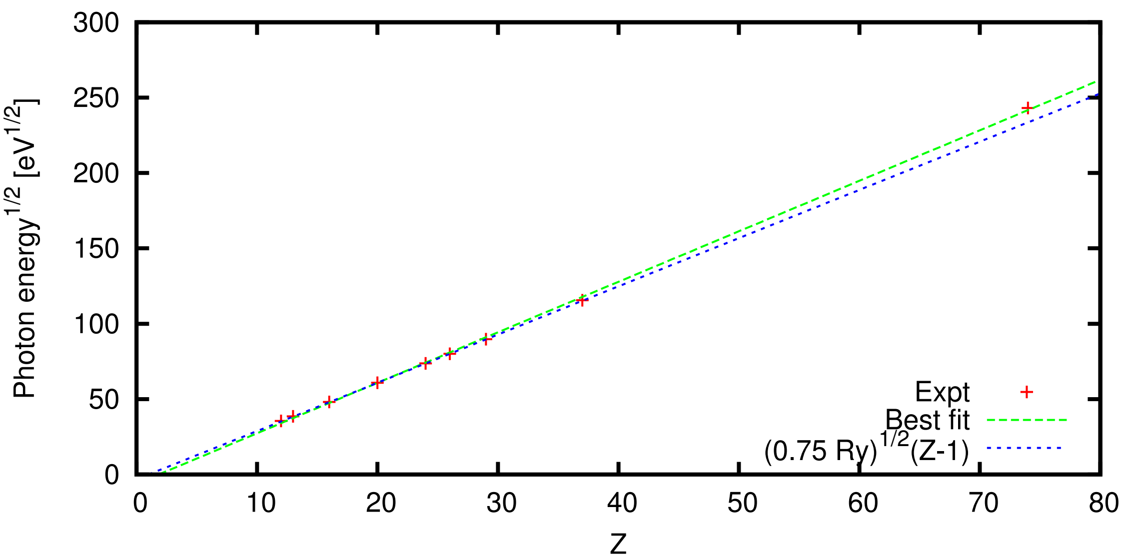
HW3 solution

MTLE-6120: Spring 2018

Due: Feb 12, 2018

1. **Kasap 3.20: X-Rays and the Moseley relation**.
   Instead of frequency ν, perform the analysis using photon energy $\hbar\omega = h\nu$ in eV instead.

   (a) Converting data in the question to photon energy in eV and plotting $\sqrt{\hbar\omega}$ vs. Z yields

   (b) Fitting the above to a straight line yields the approximate relation

   $$\sqrt{\hbar\omega} \approx (3.35\ \sqrt{\text{eV}})(Z - 1.85)$$

   i.e.

   $$\hbar\omega \approx (11.2\ \text{eV})(Z - 1.85)^2.$$

   For the hydrogen atom, the K_α line due to transition from $n = 2$ to $n = 1$ corresponds to the photon energy $-1/2^2 - (-1/1^2)$ Ry $= 0.75$ Ry $= 10.2$ eV. Durig X-ray emission form $Z > 2$ atoms, the innermost shell has 1 electron (1 missing) and the transition occurs from the next innermost shell. Both these shells would therefore experience a nuclear charge $\sim Z - 1$. Since the hydrogenic energy levels $= -Z^2/n^2$ Ry, we would expect the X-ray photon energies to be

   $$\hbar\omega \approx (10.2\ \text{eV})(Z - 1)^2,$$

   reasonably close to the best fit line.

2. **Kasap 3.27: Hund's rule**.

   The given electronic configurations for C are:

   (a) 2s(↑↓) 2p (↑, ↑,) 3s ( )

(b) 2s(↑↓) 2p (↑↓, ,) 3s ( )

(c) 2s(↑) 2p (↑↓, ↑,) 3s ( )

(d) 2s(↑) 2p (↑, ↑, ↑) 3s ( )

(e) 2s(↑↓) 2p (↑, ,) 3s (↑)

The dominant energy cost is for exciting electrons from one shell to a higher one. (a) and (b) have a fully-filled 2s shell and both remaining electrons in the next lowest 2p shell, so they will have lower energy than the rest.

Between those two, (a) has unpaired electrons and will have lower energy by Hund's rule. Similarly, (c) and (d) differ only by paired vs unpaired electrons in 2p, and (d) has lower eneryg by Hund's rule. So far, we therefore get the energy order (a) < (b) < (d) < (c).

Finally, (e) involves excitation to the higher 3s shell, while keeping the 2s shell filled. Clearly it has higher energy than (a) or (b), isnce it involves a 2p to 3s excitation relative to those. The comparison with (c) and (d) is a little trickier, since those also involve excitations relative to the ground state (a) (i.e. 2s to 2p excitations). Since the paired 2s state in (e) will have a higher repulsion energy than the unpaired ones in (c) and (d), and likely the excitation energy to the 3s shell is greater, (e) should be the highest energy.

3. **Photoemission from a δ-atom**

The δ-atom with potential $-V_0\delta(x)$ has a single bound state $e^{-\kappa|x|}\sqrt{\kappa}$ with $\kappa = mV_0/\hbar^2 \equiv q/2$ (as shown in class), and free states at any energy $E > 0$ (previous HW). Now apply a time-varying electric field $\mathcal{E}e^{-i\omega t}$ in the x direction (from an EM wave, for example).

(a) For the atom in its ground state, what is the minimum ω that can free the electron?

The bound state energy is $E = \frac{-\hbar^2\kappa^2}{2m} = \frac{-\hbar^2 q^2}{8m}$, while the lowest energy free state is $E = 0$. So the ionization potential (analagous to work-function, but for an atom/molecule) is

$$\hbar\omega_{\min} = \phi_0 = \frac{\hbar^2 q^2}{8m}.$$

(b) For the δ-atom free states solved in the previous HW, let us solve the normalization problem by assuming that the entire system is inside an infinite potential well of length L (centered at $x = 0$). What are the normalized wavefunctions and the condition(s) satisfied by the allowed k? (Hint: there are two classes of solutions: odd and even about $x = 0$. Also, you may not be able to solve for k explicitly in some cases; only write the condition satisfied by k in those cases.)

Our general solution was

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < 0 \\ Ce^{ikx} + De^{-ikx}, & x > 0 \end{cases}.$$

This time we cannot zero any of the coefficients, because reflections at the outer walls can generate all the components. Value and derivative matching yield the conditions

$$A + B = C + D,$$
$$(ikC - ikD) - (ikA - ikB) = -q(A + B).$$

Additionally, $\psi(x)$ must now be zero at $x = \pm L/2$, which yields

$$Ae^{-ikL/2} + Be^{ikL/2} = 0 \qquad \Rightarrow \qquad A = -Be^{ikL},$$
$$Ce^{ikL/2} + De^{-ikL/2} = 0 \qquad \Rightarrow \qquad D = -Ce^{ikL}.$$

Therefore, we now have four homogeneous equations in A, B, C, D.

Substituting for A and D using the latter two equations into the first two:

$$B - Be^{ikL} = C - Ce^{ikL},$$
$$(ikC + ikCe^{i}kL) - (-ikB - ikBe^{ikL}) = -q(B - Be^{ikL}).$$

The first equation gives either $B = C$ or $e^{ikL} = 1$.
First, if we take $e^{ikL} = 1$, which corresponds to $k = 2n\pi/L$, the second equation becomes $C + B = 0$. The other relations also simplify to $A = -B$ and $C = -D$. The wavefunctions are then

$$\psi(x) = \begin{cases} -Be^{ikx} + Be^{-ikx}, & x < 0 \\ -Be^{ikx} + Be^{-ikx}, & x > 0 \end{cases},$$

which altogether is $\psi(x) = -B(e^{ikx} - e^{-ikx}) = -2iB\sin(kx) = c_0 \sin(kx)$ (say), since B is arbitrary anyway. The normalization condition is $|c_0|^2 = 1/\int_{-L/2}^{L/2} \mathrm{d}x \sin^2(kx) = 2/L$ (since $kL = 2n\pi$). Therefore the normalized wavefunctions are

$$\psi(x) = \sqrt{\frac{2}{L}} \sin kx.$$

These solutions are odd about $x = 0$.
Second, if we instead take the condition $B = C$, the derivative matching equation simplifies to

$$\frac{2k}{q} = \frac{e^{ikL} - 1}{i(1 + e^{ikL})} = \tan\frac{kL}{2},$$

We cannot explicitly solve for k in this case. But, we can use the remaining conditions to write the wavefunction with a single coefficient. We have $A = -Be^{ikL}$, $C = B$ and $D = -Ce^{ikL} = -B^{eiKL}$. Therefore

$$\psi(x) = \begin{cases} -Be^{ik(x+L)} + Be^{-ikx}, & x < 0 \\ Be^{ikx} - Be^{ik(L-x)}, & x > 0 \end{cases},$$

which altogether is $\psi(x) = B(e^{ik|x|} - e^{ik(L-|x|)}) = Be^{ikL/2}(e^{ik(|x|-L/2)} - e^{ik(L/2-|x|)}) = 2iBe^{ikL/2}\sin(k(|x| - L/2)) = c_0 \sin(k(|x| - L/2))$ (say), sinc B is arbitrary anyway. The normalization constraint is

$$\begin{aligned}
1/|c_0|^2 &= \int_{-L/2}^{L/2} \mathrm{d}x \sin^2(k(|x| - L/2)) \\
&= 2\int_0^{L/2} \mathrm{d}x \sin^2(k(x - L/2)) && \text{(even about } x = 0) \\
&= 2\int_0^{L/2} \mathrm{d}y \sin^2(ky) && (y = L/2 - x) \\
&= \int_0^{L/2} \mathrm{d}y(1 - \cos ky) \\
&= \frac{L}{2} - \frac{1}{k}\sin\frac{kL}{2} \\
&= \frac{1}{k}\left(\frac{kL}{2} - \sin\frac{kL}{2}\right).
\end{aligned}$$

Thus the normalized wavefunctions are

$$\psi(x) = \sqrt{\frac{k}{\frac{kL}{2} - \sin\frac{kL}{2}}} \sin\left[k\left(|x| - \frac{L}{2}\right)\right].$$

These solutions are even about $x = 0$.
Note that in both cases above, the k are now quantized even for $E > 0$, because these states are now bound by the box of size L.

(c) What are the matrix elements $\langle\psi_f|H'|\psi_i\rangle$ of the perturbation Hamiltonian $H' = -e\mathcal{E}x$ between the bound state (initial) and the free states (final) determined above? Use $L \gg 1/k, 1/\kappa$ to simplify the integrals. (We are going to take $L \to \infty$ below.) Are there any selection rules?

The matrix elements are defined by

$$\langle\psi_f|H'|\psi_i\rangle = (-e\mathcal{E}) \int \mathrm{d}x \psi_f^*(x) x \psi_i(x)$$

where $\psi_i(x) = e^{-\kappa|x|}/\sqrt{\kappa}$ is bound state.

Now, $\psi_i(x)$ is an even function and x is odd, so $\psi_f(x)$ must be odd for the product of all three to be even. If $\psi_f(x)$ is even, the product is odd, and its integral from $-L/2$ to $L/2$ is zero. So the complicated even solutions determined above have zero matrix element! We no longer need to deal with them. This is the selection rule, which is the 1D equivalent of $\Delta l = \pm 1$ for 3D atoms.

For the simpler odd solution, the matrix element is

$$\begin{aligned}
\langle\psi_f|H'|\psi_i\rangle &= -e\mathcal{E} \int_{-L/2}^{L/2} \mathrm{d}x \sqrt{\frac{2}{L}} \sin(kx) x e^{-\kappa|x|} \sqrt{\kappa} \\
&= -e\mathcal{E} \sqrt{\frac{2\kappa}{L}} \int_{-L/2}^{L/2} \mathrm{d}x \sin(kx) x e^{-\kappa|x|} \\
&= -e\mathcal{E} \sqrt{\frac{2\kappa}{L}} \int_{0}^{L/2} \mathrm{d}x 2 \sin(kx) x e^{-\kappa x} \\
&= ie\mathcal{E} \sqrt{\frac{2\kappa}{L}} \int_{0}^{L/2} \mathrm{d}x (e^{ikx} - e^{-ikx}) x e^{-\kappa x} \\
&= ie\mathcal{E} \sqrt{\frac{2\kappa}{L}} \int_{0}^{L/2} \mathrm{d}x (e^{-(\kappa-ik)x} - e^{-(\kappa+ik)x}) x \quad \approx ie\mathcal{E} \sqrt{\frac{2\kappa}{L}} \int_{0}^{\infty} \mathrm{d}x (e^{-(\kappa-ik)x} - e^{-(\kappa+ik)x}) x
\end{aligned}$$

since the integrand from $L/2$ to ∞ is negligible when $L \gg 1/k, 1/\kappa$.

$$\begin{aligned}
\langle\psi_f|H'|\psi_i\rangle &\approx ie\mathcal{E} \sqrt{\frac{2\kappa}{L}} \left(\frac{1}{(\kappa - ik)^2} - \frac{1}{(\kappa + ik)^2} \right) \\
&= ie\mathcal{E} \sqrt{\frac{2\kappa}{L}} \frac{(\kappa + ik)^2 - (\kappa - ik)^2}{(\kappa^2 + k^2)^2} \\
&= ie\mathcal{E} \sqrt{\frac{2\kappa}{L}} \frac{4ik\kappa}{(\kappa^2 + k^2)^2} \\
&= -e\mathcal{E} \sqrt{\frac{2\kappa^3}{L}} \frac{4k}{(\kappa^2 + k^2)^2}
\end{aligned}$$

(d) Using Fermi's Golden rule, calculate the rate of photo-excitation out of the bound state. This requires summing over the final states which have separation in k that is proportional to $1/L$. Take the limit $L \to \infty$ so that this becomes an integral. Describe the frequency dependence of the photoemission rate.

The photoemission rate is

$$\begin{aligned}
\Gamma_i &= \frac{2\pi}{\hbar} \sum_f |\langle\psi_f|H'|\psi_i\rangle|^2 \delta(E_f - E_i - \hbar\omega) \\
&= \frac{2\pi}{\hbar} \sum_k \left| -e\mathcal{E} \sqrt{\frac{2\kappa^3}{L}} \frac{4k}{(\kappa^2 + k^2)^2} \right|^2 \delta\left(\frac{\hbar^2 k^2}{2m} + \frac{\hbar^2 \kappa^2}{2m} - \hbar\omega \right) \\
&= \sum_k \frac{2\pi}{L} \frac{32\kappa^3 (e\mathcal{E}k)^2}{\hbar(\kappa^2 + k^2)^4} \delta\left(\frac{\hbar^2 k^2}{2m} + \phi_0 - \hbar\omega \right)
\end{aligned}$$

Now, $k = 2n\pi/L$ with a spacing of $2\pi/L$. When $L \to \infty$, $\sum_k 2\pi/L \to \int \mathrm{d}k$.

$$\Gamma_i = \int_0^\infty \mathrm{d}k \frac{32\kappa^3 (e\mathcal{E}k)^2}{\hbar(\kappa^2+k^2)^4} \delta\left(\frac{\hbar^2 k^2}{2m} - (\hbar\omega - \phi_0)\right)$$

Substitute k and κ in terms of corresponding energies i.e. $E = \hbar^2 k^2/2m$ and $\phi_0 = \hbar^2\kappa^2/2m$.

$$\begin{aligned}
\Gamma_i &= \int_0^\infty \mathrm{d}E \frac{\sqrt{2m}}{\hbar\sqrt{E}} \frac{32\left(\frac{\sqrt{2m\phi_0}}{\hbar}\right)^3 e^2\mathcal{E}^2 \frac{2mE}{\hbar^2}}{\hbar\left(\frac{2m(E+\phi_0)}{\hbar^2}\right)^4} \delta\left(E - (\hbar\omega - \phi_0)\right) \\
&= \frac{32\hbar\phi_0^{3/2} e^2\mathcal{E}^2}{2m} \int_0^\infty \frac{\mathrm{d}E\sqrt{E}}{(E+\phi_0)^4} \delta\left(E - (\hbar\omega - \phi_0)\right) \\
&= \frac{32\hbar\phi_0^{3/2} e^2\mathcal{E}^2}{2m} \frac{\sqrt{\hbar\omega - \phi_0}}{(\hbar\omega)^4} \qquad (\hbar\omega > \phi_0) \\
&= \frac{16 e^2\mathcal{E}^2}{\hbar^3 m\omega^4} \sqrt{\phi_0^3(\hbar\omega - \phi_0)}
\end{aligned}$$

The rate is zero for $\hbar\omega < \phi_0$ (the work function), then it increases sharply with a square root dependence on the frequency relative to the threshold, reaching a maximum for $\hbar\omega = 8\phi_0/7$, and then it decreases as ω^{-4} for large frequencies.