PHYS 3317 Fall 2012
Homework 5 Helium and Periodic Table

Sam Kean wrote a NY Times best-seller on the periodic table called "The Disappearing Spoon: And Other True Tales of Madness, Love, and the History of the World from the Periodic Table of the Elements". This book makes a nice gift to both physics loving crowd and those who are 'afraid' of or even 'hate' physics (and as physics majors you have undoubtedly met those individuals!). To whet your appetite, here is an excerpt from Chapter 5, "Elements in Times of War".

> Like other staples of modern society—democracy, philosophy, drama—we can trace chemical warfare back to ancient Greece. The city-state of Sparta, laying siege to Athens in the 400s BC, decided to gas its stubborn rival into submission with the most advanced chemical technology of the time—smoke. Tight-lipped Spartans crept up to Athens with noxious bundles of wood, pitch, and stinky sulfur; lit them; and crouched outside the city walls, waiting for coughing Athenians to flee, leaving their homes unguarded. Though as brilliant an innovation as the Trojan horse, the tactic failed. The fumes billowed through Athens, but the city survived the stink bomb and went on to win the war. That failure proved a harbinger. Chemical warfare progressed fitfully, if at all, for the next twenty-four hundred years and remained far inferior to, say, pouring boiling oil on attackers. Up until World War I, gas had little strategic value. Not that countries didn't recognize the threat. All the scientifically advanced nations in the world, save one holdout, signed the Hague Convention of 1899 to ban chemical-based weapons in war. But the holdout, the United States, had a point: banning gases that at the time were hardly more powerful than pepper spray seemed hypocritical if countries were all too happy to mow down eighteen-year-olds with machine guns and sink warships with torpedoes and let sailors drown in the dark sea. The other countries scoffed at U.S. cynicism, ostentatiously signed the Hague pact, and promptly broke their word.

> Early, secret work on chemical agents centered on bromine, an energetic grenade of an element. Like other halogens, bromine has seven electrons in its outer energy level but desperately wants eight. Bromine figures that the end justifies the means and shreds the weaker elements in cells, such as carbon, to get its electron fix. Bromine especially irritates the eyes and nose, and by 1910 military chemists had developed bromine-based lacrimators so potent they could incapacitate even a grown man with hot, searing tears. Having no reason to refrain from using lacrimators on its own citizens (the Hague pact concerned only warfare), the French government collared a ring of Parisian bank robbers with ethyl bromoacetate in 1912. Word of this event quickly spread to France's neighbors, who were right to worry. When war broke out in August 1914, the French immediately lobbed bromine shells at advancing German troops. But even Sparta two millennia before had done a better job. The shells landed on a windy plain, and the gas had little effect, blowing away before the Germans realized they'd been "attacked." However, it's more accurate to say the shells had little immediate effect, since hysterical rumors of the gas tore through newspapers on both sides of the conflict. The Germans fanned the flames—blaming an unlucky case of carbon monoxide poisoning in their barracks on secret French asphyxiants, for instance—to justify their own chemical warfare program. Thanks to one man, a bald, mustached chemist who wore a pince-nez, the German gas research units soon outpaced the rest of the world's. Fritz

Haber had one of the great minds in history for chemistry, and he became one of the most famous scientists in the world around 1900 when he figured out how to convert the commonest of chemicals—the nitrogen in air—into an industrial product. Although nitrogen gas can suffocate unsuspecting people, it's usually benign. In fact, it's benign almost to the point of uselessness. The one important thing nitrogen does is replenish soil: it's as crucial to plants as vitamin C is to humans. (When pitcher plants and Venus flytraps trap insects, it's the bugs' nitrogen they're after.) But even though nitrogen makes up 80 percent of air—four of every five molecules we breathe—it's surprisingly bad at topping off soil because it rarely reacts with anything and never becomes "fixed" in the soil. That combination of plentitude, ineptitude, and importance proved a natural target for ambitious chemists.

There are many steps in the process Haber invented to "capture" nitrogen, and many chemicals appear and disappear. But basically, Haber heated nitrogen to hundreds of degrees, injected some hydrogen gas, turned up the pressure to hundreds of times greater than normal air pressure, added some crucial osmium as a catalyst, and voilà: common air transmuted into ammonia, NH_3, the precursor of all fertilizers. With cheap industrial fertilizers now available, farmers no longer were limited to compost piles or dung to nourish their soil. Even by the time World War I broke out, Haber had likely saved millions from Malthusian starvation, and we can still thank him for feeding most of the world's 6.7 billion people today.

What's lost in that summary is that Haber cared little about fertilizers, despite what he sometimes said to the contrary. He actually pursued cheap ammonia to help Germany build nitrogen explosives—the sort of fertilizer-distilled bombs that Timothy McVeigh used to blow a hole in an Oklahoma City courthouse in 1995. It's a sad truth that men like Haber pop up frequently throughout history—petty Fausts who twist scientific innovations into efficient killing devices. Haber's story is darker because he was so skilled. After World War I broke out, German military leaders, hoping to break the trench stalemate ruining their economy, recruited Haber for their gas warfare division. Though set to make a fortune from government contracts based on his ammonia patents, Haber couldn't throw away his other projects fast enough. The division was soon referred to as "the Haber office," and the military even promoted Haber, a forty-six-year-old Jewish convert to Lutheranism (it helped his career), to captain, which made him childishly proud. His family was less impressed. Haber's über alles stance chilled his personal relationships, especially with the one person who might have redeemed him, his wife, Clara Immerwahr. She also exuded genius, becoming the first woman to earn a Ph.D. from the prestigious university in Haber's hometown, Breslau (now Wroclaw). But unlike Marie Curie, a contemporary of hers, Immerwahr never came into her own, because instead of marrying an open-minded man like Pierre Curie, she married Haber. On its face, the marriage was not a poor choice for someone with scientific ambitions, but whatever Haber's chemical brilliance, he was a flawed human being. Immerwahr, as one historian puts it, "was never out of apron," and she once rued to a friend about "Fritz's way of putting himself first in our home and marriage, so that a less ruthlessly assertive personality was simply destroyed." She supported Haber by translating manuscripts into English and providing technical support on the nitrogen projects, but she refused to help on the bromine gas work.

Haber barely noticed. Dozens of other young chemists had volunteered, since Germany had fallen behind the hated French in chemical warfare, and by early 1915 the Germans had an answer to the French lacrimators. Perversely, how-

ever, the Germans tested their shells on the British army, which had no gas. Fortunately, as in the first French gas attack, the wind dispersed the gas, and the British targets—bored out of their skulls in a nearby trench—had no idea they'd been attacked.

Undeterred, the German military wanted to devote even more resources to chemical warfare. But there was a problem—that pesky Hague pact, which political leaders didn't want to break (again) publicly. The solution was to interpret the pact in an ultraconscientious yet ultimately bogus way. In signing it, Germany had agreed to "abstain from the use of projectiles, the sole object of which is the diffusion of asphyxiating or deleterious gases." So to the Germans' sophisticated, legalistic reading, the pact had no jurisdiction over shells that delivered shrapnel and gas. It took some cunning engineering—the sloshing liquid bromine, which evaporated into gas on impact, wreaked havoc with the shells' trajectory—but Germany's military-industrial-scientific complex prevailed, and a 15 cm shell filled with xylyl bromide, a caustic tearjerker, was ready by late 1915. The Germans called it *weisskreuz*, or "white cross." Again leaving the French alone, Germany swung its mobile gas units east, to shell the Russian army with eighteen thousand *weisskreuze*. If anything, this attempt was more of a debacle than the first. The temperature in Russia was so cold the xylyl bromide froze solid. Surveying the poor field results, Haber ditched bromine and redirected his efforts to its chemical cousin, chlorine. Chlorine sits above bromine on the periodic table and is even nastier to breathe. It's more aggressive in attacking other elements for one more electron, and because chlorine is smaller—each atom weighs less than half of a bromine atom—chlorine can attack the body's cells much more nimbly. Chlorine turns victims' skin yellow, green, and black, and glasses over their eyes with cataracts. They actually die of drowning, from the fluid buildup in their lungs. If bromine gas is a phalanx of foot soldiers clashing with the mucous membranes, chlorine is a blitzkrieg tank rushing by the body's defenses to tear apart the sinuses and lungs.

Because of Haber, the buffoonery of bromine warfare gave way to the ruthless chlorine phase history books memorialize today. Enemy soldiers soon had to fear the chlorine-based *grunkreuz*, or "green cross"; the *blaukreuz*, or "blue cross"; and the nightmarish blister agent *gelbkreuz*, or "yellow cross," otherwise known as mustard gas. Not content with scientific contributions, Haber directed with enthusiasm the first successful gas attack in history, which left five thousand bewildered Frenchmen burned and scarred in a muddy trench near Ypres. In his spare time, Haber also coined a grotesque biological law, Haber's Rule, to quantify the relationship between gas concentration, exposure time, and death rate—which must have required a depressing amount of data to produce. Horrified by the gas projects, Clara confronted Fritz early on and demanded he cease. As usual, Fritz listened to her not at all. In fact, although he wept, quite unironically, when colleagues died during an accident in the research branch of the Haber office, after he returned from Ypres he threw a dinner party to celebrate his new weapons. Worse, Clara found out he'd come home just for the night, a stopover on his way to direct more attacks on the eastern front. Husband and wife quarreled violently, and later that night Clara walked into the family garden with Fritz's army pistol and shot herself in the chest. Though no doubt upset, Fritz did not let this inconvenience him. Without staying to make funeral arrangements, he left as planned the next morning.

Despite having the incomparable advantage of Haber, Germany ultimately lost the war to end all wars and was universally denounced as a scoundrel nation. The international reaction to Haber himself was more complicated. In 1919,

before the dust (or gas) of World War I had settled, Haber won the vacant 1918 Nobel Prize in chemistry (the Nobels were suspended during the war) for his process to produce ammonia from nitrogen, even though his fertilizers hadn't protected thousands of Germans from famine during the war. A year later, he was charged with being an international war criminal for prosecuting a campaign of chemical warfare that had maimed hundreds of thousands of people and terrorized millions more—a contradictory, almost self-canceling legacy. Things got worse. Humiliated at the huge reparations Germany had to pay to the Allies, Haber spent six futile years trying to extract dissolved gold from the oceans, so that he could pay the reparations himself. Other projects sputtered along just as uselessly, and the only thing Haber gained attention for during those years (besides trying to sell himself as a gas warfare adviser to the Soviet Union) was an insecticide. Haber had invented Zyklon A before the war, and a German chemical company tinkered with his formula after the war to produce an efficient second generation of the gas. Eventually, a new regime with a short memory took over Germany, and the Nazis soon exiled Haber for his Jewish roots. He died in 1934 while traveling to England to seek refuge. Meanwhile, work on the insecticide continued. And within years the Nazis were gassing millions of Jews, including relatives of Haber, with that second-generation gas—Zyklon B.

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1. Spin singlet state of helium atom

Following the example given at Lecture 7, show that the spin quantum numbers corresponding to the operators $\hat{s}^2$ and $\hat{s}_z$ for the parahelium spin state,

$$|\chi\rangle_{\text{anti}} = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right),$$

are $s = 0$ and $m_s = 0$ respectively. The spin operator for the two electrons is defined as $\hat{\mathbf{s}} = \hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2$.

2. Charge densities of neon and sodium

The charge density of an atom is given by the electronic charge, multiplied by the probability density for any electron to be found at a specific radius.

(a) Suppose that the total wavefunction for an N-electron atom can be written as the product of one-particle wavefunctions, in the form

$$\psi\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N\right) = \prod_{i=1}^{N} \psi_i(\mathbf{r}_i).$$

(In this form, the electrons are treated as distinguishable particles, but the exclusion principle is (approximately) taken into account by requiring that the

allowed single-particle states are such that no more two electrons occupy the same (spatial) state.)

Show that the atomic charge density (due to the electrons) is given by

$$\rho(\mathbf{r}) = -e\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2,$$

in which the integral of the charge density gives the total electronic charge,

$$\int d^3\mathbf{r}\rho(\mathbf{r}) = \int dr\ r^2 d\Omega \rho(\mathbf{r}) = -Ne,$$

where $d\Omega$ is the solid angle element of integration. The radial charge density is

$$\rho_r(r) = \int d\Omega \rho(\mathbf{r}).$$

(b) The neon atom has the electron configuration $1s^2 2s^2 2p^6$. Assuming non-interacting electrons, calculate the atomic charge density for neon. As a crude estimate of the screening, use $Z=9$ for the $1s$ wavefunctions, $Z=7$ for the $2s$ wavefunctions, and $Z=3$ for the $2p$ wavefunctions. Plot $r^2\rho_r(r)$ vs. r in two graphs: from $r=0$ to $r=4a_0$, which shows the core electrons, and from $r=4a_0$ to $r=4a_0$ to $r=25a_0$, which shows the valence electrons. You will need table expressions for the wavefunction of H-like atom, e.g. get them from http://en.wikipedia.org/wiki/Hydrogen-like_atom#Non-relativistic_wavefunction_and_energy.

(c) Do the same thing for sodium, which has a $3s$ electron added on to the neon core, for which the effective $Z=1$. Note that the $3s$ electron extends well outside the Ne core. Alkali atoms tend to have unusually large atomic radii (Cs atom being the 'fattest' of them all).

3. Energy level transitions and selection rules

We stated without proof in lecture that optical transitions in hydrogen require $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$. More exactly, these are the selection rules for allowed *electrical dipole* transitions. It means that the atom appears as an oscillating electrical dipole when either emitting or absorbing a photon. In this problem we will explore the physics behind the selection rules using two well-known examples of 1D potentials: the simple harmonic oscillator (SHO) and the infinite potential box, see Figure 1.

(a) The first question one ought to ask is why there is a transition between two stationary energy states (here called n_1 and n_2) in the first place? If a state is truly stationary, the electron will be perfectly content to remain there indefinitely, even if the state is above ground. Indeed, any transition between two
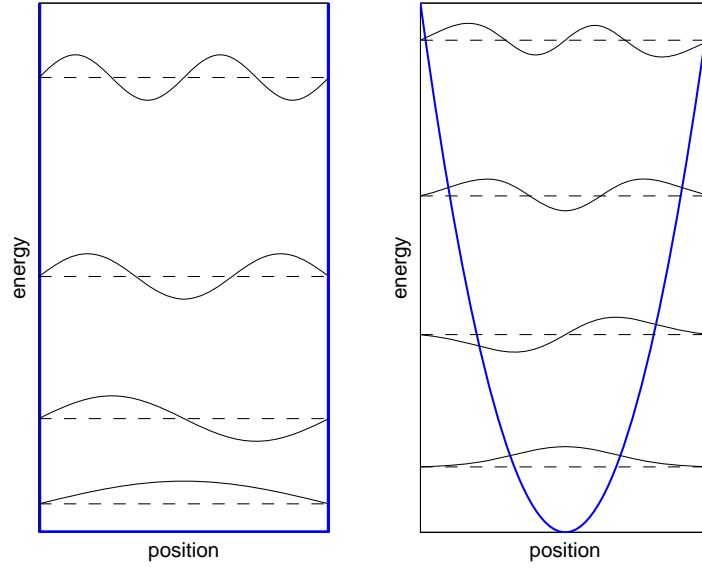
Figure 1: Infinite potential box (left) and simple harmonic oscillator (right) potentials.

stationary states requires "tickling" of the system in the form of an incoming E&M wave, which will interact with the electron via the Lorentz force. The overall Hamiltonian now includes a small time dependent part $V_{\text{int}} = V \cos(\omega t)$. PHYS4443 covers the time-dependent perturbation theory, which can be used to show that for *an allowed* transition with frequency $\omega_0 = (E_{n_2} - E_{n_1})/\hbar$ there is an oscillating probability of the system to go from state n_2 to state n_1 (and vice versa)

$$P_{n_2 \to n_1} = \frac{|V_{n_1 n_2}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2},$$

where $V_{n_1 n_2} \equiv \langle n_1 | V | n_2 \rangle$.

Figure 2 shows this probability plotted vs. time (left) for a given frequency of the "tickling" as well as the same probability vs. frequency (right) for a given time. Clearly, the tickling at the resonant ω_0 is strongly favored (in our surrounding there are *always* many frequencies present, if nothing else there are *vacuum fluctuations*, which are responsible for the so-called *spontaneous* emission). Below we investigate when $V_{n_1 n_2}$ is nonzero and therefore the radiative transition becomes possible.

(b) If the electron is to emit a photon it must act as an oscillating dipole. Stationary states proper do not qualify since they guarantee time-independence of all the observables. However, any superposition of two stationary states is a potential candidate. The electric dipole operator in 1D is simply $\hat{\mu}_e = -e\hat{x}$ (charge
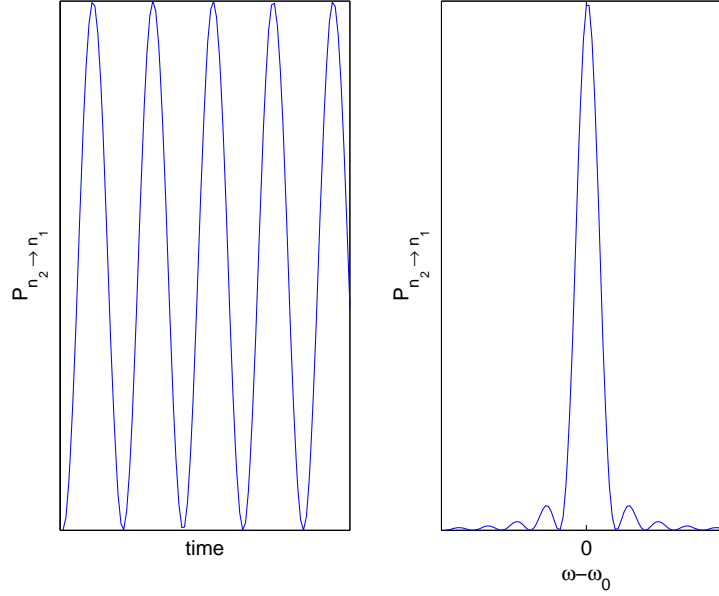
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Figure 2: Probability of $n_2 \to n_1$ transition when electron is "tickled" by an incoming E&M wave.

times separation). Thus, emission is only possible if $\langle \mu_e \rangle \equiv \langle \psi_{\text{emit}} | \mu_e | \psi_{\text{emit}} \rangle$ is a function of time for a state formed as a superposition of $|n_1\rangle$ and $|n_2\rangle$:

$$|\psi_{\text{emit}}(t)\rangle = c_1 \, |n_1(t)\rangle + c_2 \, |n_2(t)\rangle \, .$$

In other words, the electron in an atom or a potential about to emit a photon quivers between the two stationary states. But the superposition of these two stationary states ought to be able to produce time-varying electrical dipole to enable the transition. This is equivalent to writing V_{int} above in terms of the electric field $\mathcal{E}_x \cos(\omega t)$ interacting with the dipole operator $\hat{\mu}_e$ as $V_{\text{int}} = e\mathcal{E}_x \hat{x} \cos(\omega t)$. Thus, the emission in the simple 1D case is possible whenever $\langle n_1 | \mathcal{E}_x \hat{\mu}_e | n_2 \rangle \propto \langle n_1 | \hat{x} | n_2 \rangle \neq 0$. Using this information, derive the selection rules for the infinite potential box which has the familiar eigenstates:

$$\langle x | n \rangle = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x.$$

(c) Make a MATLAB function called `movie_box`, which takes two quantum numbers `n1` and `n2` as input arguments. Inside this function, prepare the transition state ψ_{emit} such that $c_1 = c_2$ in the superposition expression above. (Note: you don't need to use `schrod.m` here since you *know* the wavefunctions). Animate the state in time for a couple of oscillation cycles while plotting $|\psi_{\text{emit}}(x,t)|^2$. In your movie plot, show $\langle \hat{x} \rangle$ location as done in Figure 3 (with a red circle). Finally,

produce a plot of $\langle \hat{x} \rangle$ vs. time for `n1=1` and `n2=2,3,4` (three different plots, but you can put them on the same graph to save some paper). Is the picture consistent with your selection rules in part **(b)**? Turn in your $\langle \hat{x} \rangle$ vs. time plot(s) (turning in your MATLAB code for this homework is optional).
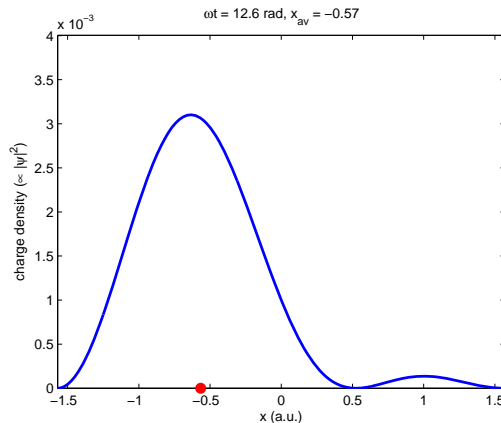

Figure 3: A snapshot example of time evolution of the "quivering" state.

(d) Now make a similar MATLAB function called `movie_sho`, which does the same for two simple harmonic oscillator state. Recall that the eigenstates of SHO are given by

$$\langle x|n \rangle = \frac{1}{\sqrt{2^n\, n!}} \left(\frac{m\omega_1}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega_1 x^2}{2\hbar}} H_n \left(\sqrt{\frac{m\omega_1}{\hbar}} x \right), \qquad n = 0, 1, 2, \ldots .$$

(Hint: since we only care about qualitative behavior, you can set physical constants to be $m = \omega_1 = \hbar = 1$ for convenience). Make the same plot of $\langle \hat{x} \rangle$ vs. time for `n1=1` and `n2=2,3,4`. Submit your plot(s). What selection rule can you infer for the quantum number n in the SHO potential?

To compute Hermite polynomials you can use `HermitePoly.m` function available on the Blackboard under *Simulations*. If `x` contains a vector of positions, the Hermite polynomial of order `n` can be evaluated at these `x` values using `polyval(HermitePoly(n),x)` command.