Problem Set 11: Chemistry
Graduate Quantum I
Physics 6572
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Potentially useful reading
Sakurai and Napolitano, sections 3.7 (central potentials), 7.3-4 (Helium)
Schumacher & Westmoreland, section 14.5 (exchange), 16.3 (Hydrogen)
Weinberg section 4.5 (periodic table)

11.1 **Periodic Table.** (Atomic) ③

In this exercise, we examine the periodic table to gain insight into the amazing but mysterious utility of thinking of electrons in atoms as filling independent orbitals.

The electron-electron repulsion in atoms, molecules, and solids is almost as large as the electron-nuclear attraction. However, in physics and chemistry we discuss many-electron systems in the language of non-interacting electrons. Thus metals and semiconductors have electron and hole excitations, atoms have 1s electrons near the nucleus and 3d electrons in the transition metals, and diamond has tetrahedral coordination because of sp^3 hybridization of the 2s/2p and 3s/3p orbitals. All of these labels would be valid if the electrons did not interact – but the true electron wavefunctions for an N-electron atom is a complex function of $3N$ variables that in no way factors into 'orbitals'.

First, let us pretend that electrons did not interact with one another: the Coulomb repulsion between electrons is set to zero. Remember that the first four angular momentum states $L = 0, 1, 2, 3$ are called s, p, d, and f for obscure historical reasons.[1] Remember also that the hydrogen spectrum has energy levels $E_n = -(1/n^2)13.6\text{eV}$, with the nth energy level including states with $L = 0, \ldots, n-1$.

(a) *How many non-interacting electrons can fit into the s, p, d, and f states? How many total electrons can fit into each level E_n? If we assume the elements in this non-interacting world kept the same names for each atomic number, which elements would be noble gases?*

These atomic levels are not just a fiction. One can use a high-energy electron or X-ray to eject an electron from an atom (creating a 'core hole' in, say, the 1s state). An electron from the 2s state may then transition into the hole, simultaneously ejecting a third 2p electron from the nucleus. This emitted particle is called an *Auger electron*.

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[1]There is yet a different notation for these states in the X-ray community (K, $L_1, \ldots, M_5$), involving also the total angular momentum $J = L + S$ of the electrons.

The kinetic energies of the Auger electrons will be given, to a good approximation, by the energy difference $-(E_{1s} - E_{2s} - E_{2p})$, just as one would expect if the electrons did not interact.[2] Auger transitions are often used to identify chemical species.

(b) *In our non-interacting world, we can have multi-electron atoms with a hydrogen nucleus. What would the energy be of the emitted Auger electron in the above transition?*

The problem here, however, is if the electrons did not interact the 1s core hole would be an eigenstate that would not decay.[3] This last point is the key to the puzzle. The eigenstates of the noninteracting electrons become *resonances* when interactions are turned on. Their energies are complex, with imaginary parts that correspond to their lifetimes – here due to their interaction with other electrons. Electrons and holes in metals and semiconductors become *quasiparticles* – quasi-electrons and quasi-holes that carry around a screening cloud or atomic polarization cloud, and decay eventually into lower-energy excitations.

The resonance energy levels of a 1s core excitation of an atom with nuclear charge Z should be roughly given by the 1s ionization energy of the corresponding helium-like two-electron ion; the outer electrons are mostly farther away from the nucleus and thus will not lower the interaction energy. But the 2s electron resonance energy will roughly be given by the 2s state for an atom with charge $Z - 2$, since the 1s electrons will partially screen the nucleus.[4] The different orbitals (1s, 2s, 2p, 3s, 3p, 3d, ...) will get shifted in energy away from their hydrogenic values because of this screening. Various approximate quantum methods for incorporating this screening energy can be developed (e.g., Hartree-Fock).

We can gain some understanding of the power of this picture, without getting buried in arcane Auger tables, by examining the periodic table. Find a periodic table that conveniently shows the fillings of the different subshells (1s, 2s, 2p, 3s, ...).

(c) *Find an ordering of the energies of the subshells that mostly explains the ground state level filling of the different atoms, up to Radon (i.e., ignoring the late radioactive ones). What are the exceptions to your rule?*

(d) *Are the noble metals closed-shell like the noble gases?*

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[2]Corrections for the interaction energy between the 2s and 2p holes in the final state, and corrections for the electronic screening energies, improve the accuracy of this rough estimate.

[3]The 2s-1s transition could happen by two-photon emission, but would not eject the other electron. Of course, allowing photon emission also makes the electronic excited states into resonances, not eigenstates. Photon emission is small because the fine structure constant $\alpha = e^2/\hbar c \sim 1/137$ is small. The electron-electron interaction is not small, which makes the question more subtle.

[4]Actually, in electronic structure calculations one often treats the core electrons with a *pseudopotential*. Instead of treating the 2s excitation of a Z atom as a 2s excitation of a $Z - 2$ atom, one treats it as a 1s excitation of a $Z - 2$ atom, but with a potential that smoothly blurs out the nucleus inside the radius of the 1s shell. They choose this smooth potential to match the scattering amplitudes of the original core-electron ion.

11.2 Chemistry with spin 3/2. (Weinberg, problem 4.7) ○

Imagine that the electron has spin 3/2 instead of 1/2, but assume that the one-particle states with definite values of n and ℓ in atoms are filled, as the atomic number increases, in the same order as in the real world. What elements with atomic numbers in the range 1 to 21 would have chemical properties similar to those of noble gases, alkali metals, halogens, and alkali earths in the real world?

11.3 Harmonic Fermi sea. (Quantum,fermions) ③

N identical spin $\frac{1}{2}$ Fermions are subject to a three-dimensional simple harmonic-oscillator potential. Ignore any mutual interactions between the particles.

(a) *Show that the change in the ground state energy when adding an additional particle jumps at certain 'magic' N. These are analogous to (but not the same as) the atomic numbers of the noble gases in atomic physics.[5] Give the first four of these magic numbers.*

The effective potential for nuclear matter is smooth near the center of the nucleus, so the magic numbers for the number of protons Z and neutrons N in the nucleus are similar to those found in the harmonic oscillator potential.

(b) *Show, if N is large, that the Fermi energy is approximately $E_F = \hbar\omega\sqrt[3]{3N}$, and the ground state energy is $E_B = (3/4)\hbar\omega\sqrt[3]{3N^4}$.*

The number of neutrons in heavy nuclei is larger than the number of protons, because it costs extra Coulomb energy to push protons into the nucleus. (Protons can turn into neutrons by emitting positrons in a β^+ decay.) But when there are more neutrons, they become more costly because their Fermi energy is higher (the Pauli exclusion principle forces them into a high-energy, unoccupied harmonic oscillator state). This is incorporated, in the high-N limit (ignoring the shell structure) into a 'Pauli term' in the semi-empirical mass formula for estimating nuclear binding energies.

(c) *If there are $Z = A/2 - \Delta/2$ protons and $N = A/2 + \Delta/2$ neutrons in a 3D harmonic oscillator of frequency $\hbar\omega$, what is the change in the ground state energy $E_B(Z, N) - E_B(A/2, A/2)$ for small Δ, to second order in Δ?*

This does not quite give the form used in the semi-empirical mass formula (Pauli energy $= -a_A(A - 2Z)^2/A$).[6] It is usual to use the free Fermi gas in a confining sphere instead of a 3D harmonic oscillator to model the nuclear potential; the latter gives a different denominator.

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[5]Noble gases are particularly stable; the binding energy of electrons filling the closed shell is unusually high, and the binding energy for the electron for the next alkali metal is unusually low. This corresponds to a jump in the energy per particle at the atomic number of the noble gas.

[6]Note that the semi-empirical mass formula gives the binding energy, which is a constant minus the ground state energy – hence the minus sign.

11.4 **Lithium ground state symmetry.** (Quantum) ③

A simple model for heavier atoms, that's surprisingly useful, is to ignore the interactions between electrons (the *independent electron* approximation).[7]

$$\mathcal{H}^Z = \sum_{i=1}^{Z} p_i^2/2m - k_\varepsilon Z e^2/r_i \tag{1}$$

Remember that the eigenstates of a single electron bound to a nucleus with charge Z are the hydrogen levels ($\psi_n^Z = \psi_{1s}^Z, \psi_{2s}^Z, \psi_{2p}^Z, \dots$), except shrunken and shifted upward in binding energy (E^Z more negative):

$$\mathcal{H}^Z \psi_n^Z = E_n^Z \psi_n$$
$$\psi_n^Z(\mathbf{r}) = \psi_n^H(\lambda_r \mathbf{r})$$
$$E^Z = \lambda_E E^H \tag{2}$$

(a) *By what factor λ_r do the wavefunctions shrink? By what factor λ_E do the energies grow?* (Hint: Dimensional arguments are preferred over looking up the formulas.)

In the independent electron approximation, the many-body electron eigenstates are created from products of single-electron eigenstates. The Pauli exclusion principle (which appears only useful in this independent electron approximation) says that exactly two electrons can fill each of the single-particle states.

(b) *Ignoring identical particle statistics, show that a product wavefunction*

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots) = \psi_{n_1}^Z(\mathbf{r}_1)\psi_{n_2}^Z(\mathbf{r}_2)\psi_{n_3}^Z(\mathbf{r}_3)\dots \tag{3}$$

has energy $E = \sum_i E_{n_i}^Z$.

The effect of the electron-electron repulsion in principle completely destroys this product structure. But for ground-state and excited-state quantum numbers, the language of filling independent electron orbitals is quite useful.[8] However, the energies of these states are strongly corrected by the interactions between the other electrons.

(c) *Consider the 2s and 2p states of an atom with a filled 1s shell (one electron of each spin in 1s states). Which state feels a stronger Coulomb attraction from the nucleus? Argue heuristically that the 2s state will generally have lower (more negative) energy*

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[7]Here $k_\varepsilon = 1$ in CGS units, and $k_\varepsilon = 1/(4\pi\varepsilon_0)$ in SI units. We are ignoring the slight shift in effective masses due to the motion of the nucleus.

[8]The excited states of an atom aren't energy eigenstates, they are *resonances*, with a finite lifetime. If you think of starting with the independent electron eigenstates and gradually turning on the Coulomb interaction and the interaction with photons, the true ground state and the resonances are adiabatic continuations of the single-particle product eigenstates – inheriting their quantum numbers.

and fill first.

It is often true, if two particles or systems are non-interacting, that their wavefunctions factor (much like separation of variables). In the absence of spin-orbit scattering (a relativistic effect which is small for light atoms), the Hamiltonian splits into a spin and spatial piece, with no interactions. Can the wavefunction of Lithium, ignoring the small spin-orbit scattering, be factored be factored into a spatial and a spin piece?

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \mathbf{r}_3, s_3; \dots) \stackrel{?}{=} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \dots)\chi(s_1, s_2, s_3 \dots) \qquad (4)$$

We'll check this in the first non-trivial case – the lithium atom ground state, in the independent electron approximation. From part (c), we know that two electrons should occupy the 1s orbital, and one electron should occupy the 2s orbital. The two spins in the 1s orbital must be antiparallel; let us assume the third spin is pointing up $\uparrow_3$:

$$\Psi^0(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \mathbf{r}_3, s_3) = \psi_{1s}^{\mathrm{Li}}(\mathbf{r}_1)\psi_{1s}^{\mathrm{Li}}(\mathbf{r}_2)\psi_{2s}^{\mathrm{Li}}(\mathbf{r}_3)\,\uparrow_1\downarrow_2\uparrow_3. \qquad (5)$$

But we're not done: this combination is not antisymmetric under permutations of the electrons.

(d) *Antisymmetrize Ψ^0 with respect to electrons 1 and 2. Show that the resulting state is a singlet with respect to these two electrons. Antisymmetrize Ψ^0 with respect to all three electrons (a sum of six terms). Does it go to zero (in some obvious way)? Can it be written as a product as in eqn 4?*

11.5 **Photon density matrices.** (Density Matrices) ③

Consider polarized light in a basis where the vertically polarized photon is $|V\rangle = \left(\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right)$ and the horizontally polarized photon is $|H\rangle = \left(\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}\right)$

(a) *Write the density matrix $\boldsymbol{\rho}_{\mathrm{vert}}$ for a vertically polarized photon $|V\rangle$. Write the density matrix $\boldsymbol{\rho}_{\mathrm{diag}}$ for a diagonally polarized photon, $|\mathrm{diag}\rangle = (1/\sqrt{2}, 1/\sqrt{2})$.*

A beam of vertically polarized photons is incoherently mixed with a beam of diagonally polarized photons of the same frequency and wavenumber, with half of the photons coming from each beam.

(b) *What is the density matrix $\boldsymbol{\rho}_{\mathrm{merge}}$ describing a photon in the resulting beam? What is the trace of $\boldsymbol{\rho}_{\mathrm{merge}}^2$? Is it a pure state?*

Vertically polarized and diagonally polarized photons with the same wavevector are not orthogonal states. Once mixed, they are indistinguishable from a number of other mixtures (which all share the same density matrix $\boldsymbol{\rho}_{\mathrm{merge}}$.) In particular, because we have a two-dimensional set of states, we can always write $\boldsymbol{\rho}_{\mathrm{merge}}$ as a mixture of two suitably-chosen orthonormal states $|e_1\rangle$ and $|e_2\rangle$, with probabilities p_1 and p_2:
$$\boldsymbol{\rho}_{\mathrm{merge}} = p_1|e_1\rangle\langle e_1| + p_2|e_2\rangle\langle e_2| = \left(\begin{smallmatrix} p_1 & 0 \\ 0 & p_2 \end{smallmatrix}\right).$$

(c) *What are p_1 and p_2 for $\boldsymbol{\rho}_{\text{merge}}$?* (Hints: you need not solve for $|e_1\rangle$ and $|e_2\rangle$. If you like, check your answer by writing $\text{Tr}(\boldsymbol{\rho}_{\text{merge}})$ and $\text{Det}(\boldsymbol{\rho}_{\text{merge}})$ in terms of p_1 and p_2, and checking that they are unchanged by the change of basis from vertical/horizontal to $|e_1\rangle$, $|e_2\rangle$.)

When we merge the beams, we lose information about the photons, increasing the entropy of the universe.

(d) *What is the entropy gain ΔS per photon? For ease of grading, please write your answer in terms of p_1 and p_2.* (Hint: The entropy per photon is $S = -k_B \text{Tr}(\rho \log \rho)$. Pure states have zero entropy. The calculation is straightforward in the basis $\{|e_1\rangle, |e_2\rangle\}$, and you needn't solve for the new basis eigenstates.)

11.6 **Nuclear Shell Model.** (nuclear) ③

Nuclear physics is challenging. Unlike atomic physics, where the interaction of electromagnetism with matter is weak (of order $\alpha = 1/137$), the interaction between quarks (and hence nucleons) is strong – so we cannot use perturbation theory. Unlike condensed matter physics, where we can assume many particles and hence describe liquids and crystals with continuum theories, the number of protons and neutrons in a nucleus is relatively small.

Nuclear physics is thus a field where creative use of simple models is widespread. We have explored earlier the use of *random matrix theory* to describe excitations of nuclei. In this exercise, we shall introduce both the *nuclear shell model* and the nuclear *semi-empirical mass formula*.

We shall use real data, downloaded directly from the Web. There is a table of atomic masses of various isotopes at the Atomic Mass Data Center, http://amdc.in2p3.fr/masstables/Ame2011int/mass.mas114.

(a) *Download the mass table directly into your computational environment. After reading them, drop the first 39 lines of header. For each N and Z in the table with experimental data[9] make a table of the nuclear names (e.g., 56Fe) and of the 'mass excess' column (converted to floats). The mass excess is the atomic mass minus one amu (atomic mass unit) per nucleon, where an amu = 931.494061 MeV is one-twelfth the energy of ^{12}C. The semi-empirical mass formula estimates the nuclear mass, which means we need to add back $A \times$ amu and subtract the Z electron masses m_e. Store the binding energy indexed by Z and N:*

$$\text{nuclear mass} = \text{mass excess} + A\,\text{amu} - Zm_e. \tag{6}$$
$$\text{binding energy} = Zm_p + Nm_n - \text{nuclear mass}. \tag{7}$$

Create a matrix with these entries (zero where no experimental data), and make a plot of the non-zero entries.[10]

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[9]Warning: data with # instead of decimal points are theoretical extrapolations. Drop those points.

[10]You can use a *masked array* to do this in Python; in Mathematica you can set ColorRules → 0.0→White.

(Hint: the main feature of this plot will be that larger A have larger nuclear masses.)

The semi-empirical mass formula treats the nucleus primarily as a drop of liquid, with a 'condensation energy' $a_V A$, where $A = N + Z$ is the number of nucleons, and a surface tension energy $a_S A^{2/3}$. (If the nucleus is a liquid of nucleons of roughly constant density, then its radius $R \sim A^{1/3}$ and hence the surface area $\sim R^2 \sim V^{2/3}$.) Packing Z protons into the nucleus costs a Coulomb energy (as in $(Zq)^2/R$) of $-a_C Z^2/A^{1/3}$; this Coulomb energy is why there are more neutrons than protons in heavy nuclei.

In addition, there are two quantum terms. The first is the Pauli term, which is related to exercise (3); if the number of neutrons N is different than the number of protons Z, the neutron Fermi energy will be different than the proton Fermi energy, and there will be a energy cost that grows as the difference. Since either positive or negative differences will reduce the binding energy,[11] it is natural to approximate this difference with the square $(N - Z)^2$. It turns out that the magnitude of this effect grows weaker as A grows, so using $A = N + Z$ we approximate the Pauli energy $-a_A(N-Z)^2/A = -a_A(A-2Z)^2/A$.

The second quantum term is a pairing energy. If the number of protons (or neutrons) is even, the energy is lower than if it is odd, by a pairing energy that goes roughly as $\delta = a_P/A^{1/2}$. (Some sources say this is due to the fact that the second nucleon can 'go into the same orbital' as the first; others say this even-odd term is due to spin-orbit interactions; others blame it on the formation of superconducting Cooper pairs of protons or neutrons.) The pairing energy is considered zero for even-odd nuclei, positive (binding) for even-even nuclei, and negative (destabilizing) for odd-odd nuclei. (It is interesting to note that there are only four stable nuclei with an odd number of protons and an odd number of neutrons.)

We use Rohlf's values (Rohlf: Modern Physics from a to Z0, James William Rohlf, Wiley, 1994, section 11.3, quoted from Wikipedia), who give $a_V = 15.75\,\text{MeV}$, $a_S = 17.8\,\text{MeV}$, $a_C = 0.711\,\text{MeV}$, $a_A = 23.7\,\text{MeV}$, and $a_P = 11.18\,\text{MeV}$.

(b) *Create a function SemiEmpiricalMassFormula(Z,N) that evaluates this formula. Check against the actual value for 56Fe from your calculation in part (a).*[12] (Hint: Iron has $Z = 26$ and hence $^5 6$Fe has $N = 30$. Your answer should be within less than a percent of the experimental value. This can also help debug part (a). For assistance in checking for typos, I got volumeTerm=882.0 MeV, surfaceTerm=-260.54 MeV, coulombTerm=-125.628 MeV, PauliTerm=-6.77 MeV, δ=1.49 MeV.)

One major piece of physics that the semi-empirical mass formula misses are the *magic numbers*. These are explained by assuming that, like atoms, the nucleons approximately fill 'orbitals' that have 'shells' (like the 1s, 2s, 2p, ... for atoms). Just as noble gases arise when a shell fills and the next orbital has a big jump in energy, so nuclei have especially stable states. Notice, though, that there is only one type of electron, while

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[11]Usually there will be more neutrons

[12]Iron 56 is one of the most stable nuclei. It dominates the endpoint of fusion reactions in stars. Lower mass nuclei tend to fuse; higher masses tend to fission. I hear that $^6 2$Ni is even more stable, but isn't accessible easily in nuclear reactions.

there are two types of nucleons. So we expect especially stable nuclei when either the proton or the neutron number is magic: horizontal or vertical bands in a color plot of mass versus Z and N.

(c) *Make a 2D color plot of the difference between the semi-empirical mass formula and the actual binding energy, as a grid of Z versus N. Don't plot colors (or plot white) where experimental data is not available.[13] Note the horizontal and vertical bands where the theory underestimates the binding energy. Estimate these 'magic numbers'. Do your estimates agree with the Harmonic Fermi sea estimates of an earlier exercise? Do they agree with Wikipedia's list 2, 8, 20, 28, 50, 82, 126?*

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[13]You can use a *masked array* to do this in Python; in Mathematica you can set ColorRules → 0.0→White.