ICFP M1 - QUANTUM MATTER - TD n°5 - Exercises
Spin-orbit coupling

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1 Derivation of the spin-orbit interaction from Dirac's equation

You might have seen or will see in an advanced quantum mechanics or field theory class, that the proper description of a spin-1/2 particle is given by Dirac's equation, which includes also the description of the antiparticle (in Dirac's equation the particle and antiparticle sectors couple). In the large rest-mass energy limit (appropriate for condensed matter, it is the non-relativistic limit), we can effectively decouple the two sectors, provided we include some effects which remain in the pure particle sector. One of them is spin-orbit coupling. The idea is to expand Dirac's equation with Coulomb interactions in the small $W = E - mc^2 \ll mc^2$ limit (mc^2 is the rest energy, c is the speed of light), which we will do here.

For a particle of charge q, mass m, moving in potential $(\phi, \mathbf{A})$, the stationary form of the Dirac Hamiltonian given by $\hat{H}\psi = E\psi$,

$$\hat{H} = \begin{pmatrix} (mc^2 + q\phi)\mathrm{id}_2 & c\sigma \cdot (\hat{\mathbf{p}} - q\mathbf{A}) \\ c\sigma \cdot (\hat{\mathbf{p}} - q\mathbf{A}) & (-mc^2 + q\phi)\mathrm{id}_2 \end{pmatrix}. \tag{1}$$

Note that this is a 4×4 matrix.

1. Consider the bispinor (essentially a four-component vector) $\psi^T = (\psi_a, \psi_b)$. Write the two ($2 \times 2$ coupled equations for ψ_a, ψ_b).

2. Using the second row equation, express ψ_b in terms of ψ_a and trade E for the shift to the rest-mass energy $W = E - mc^2$ (recall E is the eigenenergy). In the non-relativistic limit, $W, q\phi \ll mc^2$, obtain ψ_b as a function of ψ_a at leading order.

3. Define $V = q\phi$ and substitute into the first equation, to obtain the "Pauli equation" $\hat{H}_{\mathrm{NR}}\psi_a = W\psi_a$ ("NR" stands for "nonrelativistic"). Expand the square using Pauli matrix identities to find a more familiar expression.

4. Interpret each term. Identify the spin magnetic moment $\boldsymbol{\mu}_S$.

5. Now we find the leading spin-orbit coupling term. To do so, take $\mathbf{A} = \mathbf{0}$ for simplicity, and expand ψ_b in terms of ψ_a up to the next order in $W, q\phi \ll mc^2$.

6. Now you can find the effective Hamiltonian at that order and identify the spin-orbit coupling term $H_{\mathrm{s.o.}}$.

7. Assume the potential is approximately radial (e.g., near the atoms), and rewrite $H_{\mathrm{s.o.}}$ in that case.

2 Aufbau principle and Hund's rules

You reviewed in the lecture what the solutions to the hydrogen atom were. Central to the derivation was the fact that there was a unique electron, and hence no electron-electron interactions. In most atoms/ions, this is not the case, and an exact solution is not accessible.

In the simplest non-trivial approximation (the Hartree approximation), we assume that a given electron moves in a potential $V_{\mathrm{eff}}(\mathbf{r})$ resulting from the nucleus and from the averaged charge density due to the other electrons. Due to the isotropy of space, $V_{\mathrm{eff}}(\mathbf{r})$ has spherical symmetry, and for a given electron, we solve the single-particle Schrödinger equation. The resulting eigenfunctions take the same form as those of the hydrogen atom

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi), \tag{2}$$

as one finds from a separation ansatz, labeled by quantum numbers $n \in \{1, 2, 3, \cdots\}$, $l \in \{0, 1, 2, \cdots, n-1\}$, and $m \in \{-l, -l+1, ..., l\}$. The angular part is identical for any spherically symmetric potential and is given by the spherical harmonics $Y_{lm}(\theta, \phi)$. The associated bound state energy eigenvalues for the hydrogen atoms were $E_{nl}^{\mathrm{H}} = -e^2/(2na_{\mathrm{B}})$, where $a_{\mathrm{B}} = \hbar^2/(me^2) = 0.529$ rA is the Bohr radius, and depended only on the principal quantum number n, so that there were $2\sum_{l=0}^{n-1}(2l+1) = 2n^2$ (accounting

(a)   (b)   (c)
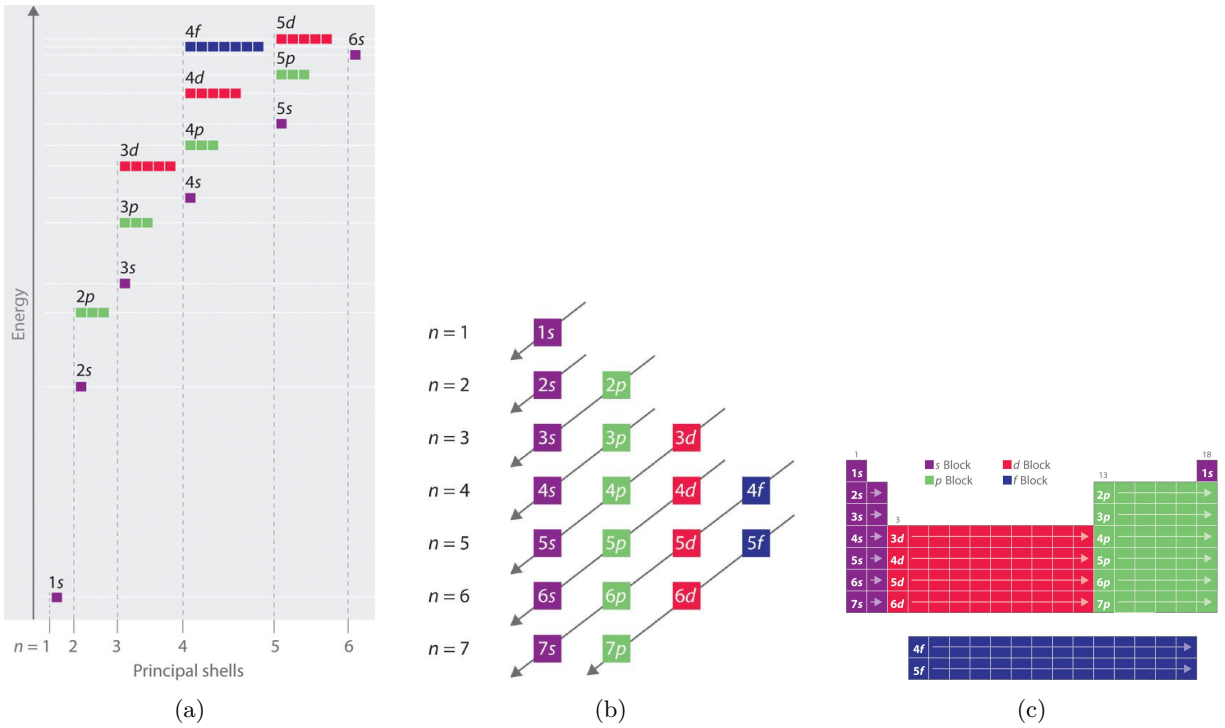
Figure 1: Figures from Chem Libre Text. (a) Orbital energy level diagram for a typical *multielectron* atom. (b) Diagonal rule corresponding to the energies in Fig. (a). Predicting the order in which orbitals are filled in multielectron atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left. (c) The periodic table, showing how the elements are grouped according to the kind of subshell (s, p, d, f) being filled with electrons in the valence shell of each element.
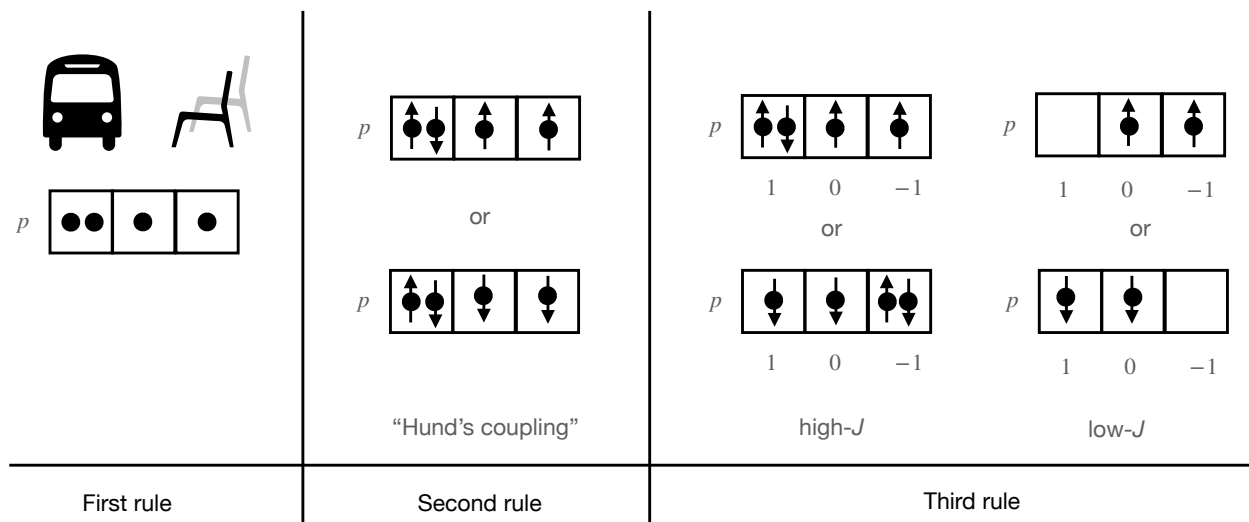

Figure 2: Sketch of Hund's rules in the case of p electrons.

also for $m_s = \pm 1/2$) degenerate states for every n. Accounting for electron-electron interactions using the Hartree method as described above introduces the essential physics of screening, a result of which is that states of different l for a given n are no longer degenerate, and E_{nl} depends on n, l. Thus E_{nl} is $2(2l + 1)$-fold degenerate for every n, l (including a factor of 2 from the spin $m_s = \pm 1/2$), each state in this degenerate manifold being labeled by m and m_s. This group of orbitals is called a **shell**, and one can argue that smaller l means lower energy since those states are localized closer to the nucleus, where the potential is less screened.

Based on the Hartree-Fock energy levels, the order in which the electron shells are filled throughout the periodic table is roughly given what is known as the **Aufbau principle** from the German Aufbau = "building up". The order in which the orbitals are filled roughly follows the diagonal rule, which says that orbitals with lower values of $n + l$ are filled before those with higher values, and that in the case of equal $n + l$ values, the orbital with the lower n is filled first.[1]

However, this electronic configuration does not uniquely specify a ground state. If a shell contains n_{nl} electrons there are $C_{2(2l+1)}^{n_{nl}}$ possible ways to distribute these electrons, which gives the degeneracy of the *many-particle state*. [Note that for a filled shell we get $C_{2(2l+1)}^{2(2l+1)} = 1$, i.e., no degeneracy.] Consider, for example, carbon, whose configuration is $1s^2 2s^2 2p^2$. The filled $1s$ and $2s$ shells are inert. However, there are $C_6^2 = 15$ possible ways to put two electrons in the $2p$ shell.

The $C_{2(2l+1)}^{n_{nl}}$-fold degenerate state splits into **multiplets** with fixed L and S and degeneracies $(2L + 1)(2S + 1)$ ($\mathbf{L} = \sum_i \mathbf{l}_i$, $\mathbf{S} = \sum_i \mathbf{s}_i$) without spin-orbit coupling. It is standard to abbreviate each such multiplet with the label $^{2S+1}L_J$, called a **term**, where $L = S, P, D, F, G, H$, etc, and $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is the total angular momentum. Typical energy splittings between multiplets are of the order of 10 eV.

The addition of angular momentum in quantum mechanics is technical and we won't discuss here because our situation will soon be simpler. But for exemple, for carbon, the largest L value we can get is $L = 2$, which requires $S = 0$ and hence $J = L = 2$. This 5-fold degenerate multiplet is then abbreviated $^1D_2$. But we can also add together two $l = 1$ states to get total angular momentum $L = 1$ as well. The corresponding spatial wavefunction is antisymmetric, hence $S = 1$ in order to achieve a symmetric spin wavefunction. Since $|L - S| \leq J \leq |L + S|$, we have $J = 0$, $J = 1$, or $J = 2$ corresponding to multiplets $^3P_0$, $^3P_1$, and $^3P_2$, with degeneracy 1, 3, and 5, respectively. The final state has $J = L = S = 0$: $^1S_0$. The Hilbert space is then spanned by two $J = 0$ singlets, one $J = 1$ triplet, and two $J = 2$ quintuplets: $0 \oplus 0 \oplus 1 \oplus 2 \oplus 2$. That makes 15 states. Which of these is the ground state?

The ground-state multiplet is found from the *empirical* **Hund's rules**.

(i) The first Hund rule is: The LS multiplet with the largest S has the lowest energy. One prefers large S because this makes the spin part of the wavefunction maximally symmetric, which means that the spatial part is maximally antisymmetric (Pauli principle). Electrons, which repel each other (Coulomb repulsion), prefer to exist in a spatially antisymmetric state. We can carry out a small calculation to "show" this might be correct.

1. recall the form of the Coulomb interaction in second quantization

   In a different (discrete) basis (not defined here, but also assumed localized), then the Coulomb interaction contains terms with the slightly modified form:

$$H' = \sum_{mnrs} U_{mnrs} c_{m\sigma}^\dagger c_{n\sigma'}^\dagger c_{r\sigma'} c_{s\sigma}, \tag{3}$$

   with

$$U_{mnrs} = \frac{1}{2} \int dx \int dx' \psi_m^*(x) \psi_n^*(x') \frac{e^2}{|x - x'|} \psi_r(x') \psi_s(x), \tag{4}$$

   with $c_{n\sigma} = \int dx \psi_n(x) c_\sigma^\dagger(x)$ and $c_{n\sigma}^\dagger |\Omega\rangle = |\psi_n\rangle = \int dx |x\rangle\langle x|\psi_n\rangle$, with $|x\rangle = c_\sigma^\dagger(x)|\Omega\rangle$.

2. What do the "direct terms," i.e. those with $r = n, s = m$, $U_{mnnm} \equiv V_{mn}$ look like?

3. How about those with $r = m, s = n$, $U_{mnmn} \equiv J_{mn}^F$?

   Note that this is a *ferromagnetic* coupling. It is thought not to be very important from atom to atom, but important within an atom.

4. How would you write a phenomenological Hamiltonian which prefers maximal S?

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[1] There are hiccups here and there. For example, in filling the 3d shell of the transition metal series (row four of the periodic table) , ^{21}Sc, ^{22}Ti, and ^{23}V, are configured as [Ar] 4s² 3d¹, [Ar] 4s² 3d², and [Ar] 4s² 3d⁴, respectively, but chromium's (Cr) (dominant) configuration is [Ar] 4s¹ 3d⁵. Similarly, copper (Cu) is [Ar] 4s¹ 3d¹⁰ rather than the expected [Ar] 4s² 3d⁹. For palladium (Pd), the diagonal rule predicts an electronic configuration [Kr] 5s² 4d⁸ whereas experiments say it is [Kr] 5s⁰ 4d¹⁰. This shell configuration stuff should not be taken too seriously, because the atomic ground states are really linear combinations of different shell configurations, so we should really think of these various configurations as being the dominant ones among a more general linear combination of states (in other words, in reality, the ground state is not a single Slater determinant and involves linear combinations of different configurations). For example, the largest weights are for Cr and Cu configurations with only one 4s electron. Zinc terminates the 3d series, after which we get orderly filling of the 4p orbitals. Row five pretty much repeats row four, with the filling of the 5s, 4d, and 5p shells. In row six, the lanthanide (4f) series interpolates between the 6s and 5d shells, as the 5f actinide series interpolates in row seven between 7s and 6d.

(ii) The second Hund rule is: If the largest value of S is associated with several multiplets, the multiplet with the largest L has the lowest energy. There really is not a specific calculation to understand the second Hund's rule, but the rationale is that large L expands the electron cloud somewhat, which also keeps the electrons away from each other (classical picture: the electrons have aligned angular momenta, i.e., rotate in the same direction, and are thus further apart).

(iii) The third Hund's rule refers to spin-orbit coupling and says: If an incomplete shell is not more than half-filled, then the lowest energy state has $J = |L - S|$. If the shell is more than half-filled, then $J = L + S$. This rule can be "justified" using the expression for the spin-orbit coupling term $H_{s.o.}$ as you derived from the expansion of the Dirac equation. We will not do it here, but you can find it for example in *Lectures on quantum mechanics* by G. Baym, Chapter 20. When this applies (lighter atoms), it is called the "l-s scheme" (or Russel-Saunders scheme). When atoms are heavy, spin-orbit coupling is strong and one should use the "j-j scheme" whereby one first addresses the spin-orbit coupling terms.

Let us now apply these rules. Here is an example:

P: The electronic configuration for elemental phosphorus is $3s^2\, 3p^3$. The unfilled 3d shell has three electrons. First maximize S by polarizing all spins parallel (up, say), yielding $S = 3/2$. Next maximize L consistent with Pauli exclusion, which says $L = -1 + 0 + 1 = 0$. Finally, since the shell is exactly half-filled, and not more, $J = |L - S| = 2$, and the ground state term is $^4S_2$.

5. Find the ground state of Mn^{4+}: $4s^0\, 3d^3$.

6. Find the ground state of Fe^{2+}: $4s^0\, 3d^6$.

7. Find the ground state of Nd^{3+}: $6s^0\, 4f^3$.

A final note: Regarding magnetism, note that completely filled shells (made up of all orbitals with the same quantum numbers (n, l) have $\langle \mathbf{l}_i \rangle = \mathbf{0}$ and and $\langle \sum_i \mathbf{s}_i \rangle = \mathbf{0}$, i.e., vanishing total angular momentum, since for each electron there is another one with opposite $\langle \mathbf{l}_i \rangle$, $\langle \mathbf{s}_i \rangle$. Clearly, the total magnetic moment of filled shells also vanishes. Thus magnetic ions require incompletely filled shells.