

Exercise 1. Hund's Rules

Hund's rules are a set of three empirical rules that allow to determine the electronic configuration of the ground state of multi-electron atoms.

The notation used to identify the state is $(2S+1)L_J$, where S , L are respectively the total spin and orbital angular momenta, and $J = L + S$. According to the spectroscopic notation the possible values of the L quantum number are identified by the letters $L = S, P, D, F, G, \dots$ for $L = 0, 1, 2, 3, 4, \dots$.

Use the Hund's rules to find the ground states of Nitrogen (N), Aluminium (Al) and Titanium (Ti) starting from the electronic configuration that you can find on any periodic table.

Exercise 2. Second order time dependent perturbation theory

The time evolution of a quantum state can be decomposed as always as:

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-i E_n^{(0)} t/\hbar} |\psi_n^{(0)}\rangle. \quad (1)$$

In time-dependent perturbation theory we can determine the coefficients $c_n(t)$ as series expansion as:

$$c_n(t) = c_n^{(0)}(t) + c_n^{(1)}(t) + c_n^{(2)}(t) + \dots \quad (2)$$

The order- j correction to the coefficient c_n fulfills the following differential equation:

$$\frac{\partial c_n^{(j)}(t)}{\partial t} = \frac{1}{i\hbar} \sum_k V_{nk}(t) e^{i\omega_{nk}t} c_k^{(j-1)}(t), \quad (3)$$

where $\omega_{nk} = (E_n^{(0)} - E_k^{(0)})/\hbar$.

(a) Knowing the expression of the first order coefficient:

$$c_n^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^t V_{ni}(\tau) e^{i\omega_{ni}\tau} d\tau, \quad (4)$$

show that the second order correction $c_n^{(2)}(t)$ can be written as:

$$c_n^{(2)}(t) = \frac{1}{(i\hbar)^2} \frac{1}{2} \sum_k \int_{t_0}^t d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 T\{V_{nk}(\tau_1) e^{i\omega_{nk}\tau_1}, V_{ki}(\tau_2) e^{i\omega_{ki}\tau_2}\}, \quad (5)$$

where we introduced the *time ordered product* T :

$$T\{\mathcal{O}(t_1), \mathcal{O}(t_2)\} = \theta(t_1 - t_2) \mathcal{O}(t_1) \mathcal{O}(t_2) + \theta(t_2 - t_1) \mathcal{O}(t_2) \mathcal{O}(t_1), \quad (6)$$

and θ is the Heaviside function.

(b) How could this reasoning be generalized to find a compact expression for the coefficient $c_n(t)$ obtained "resumming" the whole perturbative series?

Exercise 3. *Hydrogen Atom in an Electric field*

Consider a hydrogen atom in its ground state. A uniform electric field aligned along the positive z direction is turned on at $t = 0$.

Compute the probability to find the atom in each of the following states at $t = t_f > 0$.

- (a) $n = 1, l = 0$
- (b) $n = 2, l = 1, m_l = -1$
- (c) $n = 2, l = 1, m_l = 0$
- (d) $n = 2, l = 1, m_l = +1$.

You can use the following expressions for the wave functions Ψ_{nlm} :

$$\begin{aligned}\Psi_{100} &= 2 \left(\frac{1}{a}\right)^{3/2} e^{-r/a} Y_0^0(\theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a}\right)^{3/2} e^{-r/a} \\ \Psi_{21-1} &= \frac{1}{2\sqrt{6}} \left(\frac{1}{a}\right)^{3/2} \left(\frac{r}{a}\right) e^{-r/(2a)} Y_1^{-1}(\theta, \phi) = \frac{1}{8\sqrt{\pi}} \left(\frac{1}{a}\right)^{3/2} \left(\frac{r}{a}\right) e^{-r/2a} \sin \theta e^{-i\phi} \\ \Psi_{210} &= \frac{1}{2\sqrt{6}} \left(\frac{1}{a}\right)^{3/2} \left(\frac{r}{a}\right) e^{-r/(2a)} Y_1^0(\theta, \phi) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a}\right)^{3/2} \left(\frac{r}{a}\right) e^{-r/2a} \cos \theta\end{aligned}$$