Solutions of Homework # 6

Exercise 1: Hydrogen atom in a magnetic field

1. In the presence of the uniform magnetic field B along the $\hat{z}$ direction, the electronic Hamiltonian of a hydrogen atom reads:

$$\hat{H} = \hat{H}_0 + \frac{\mu_B}{\hbar}(\hat{L}_z + 2\hat{S}_z)B = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{r} + \frac{\mu_B}{\hbar}(\hat{L}_z + 2\hat{S}_z)B, \tag{1}$$

where $\hat{H}_0$ is the Hamiltonian of the unperturbed hydrogen atom, where μ is the electron reduced mass (i.e. $1/\mu = 1/M_p + 1/m_e$, where M_p is the protono mass and m_e is the electron mass[1]), and r is the radial distance between the electron and the nucleus. We know that for an electron in a central potential it is convenient to adopt spherical coordinates, where ∇^2 is made of a radial term and a term proportional to $\hat{L}^2$ (see lecture notes/slides):

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hat{L}^2}{2\mu r^2} - \frac{e^2}{r} + \frac{\mu_B}{\hbar}(\hat{L}_z + 2\hat{S}_z)B. \tag{2}$$

The angular momentum $\hat{L}_z$ commutes with the full Hamiltonian: it commutes with any radial operator (they act on different coordinates), it commutes with $\hat{L}^2$ (see commutation relations on lecture notes/slides), and also with the interaction term as $\hat{L}_z$ commutes with itself and with the spin operator $\hat{S}_z$ (they act on different subspaces/coordinates).

2. Given that $\hat{L}_z$ commutes with the full Hamiltonian, the eigenstates of the unperturbed hydrogen atom are also eigenstates in presence of the field B. However, the energy eigenvalues change and now they also depend on the "magnetic" quantum number m:

$$\hat{L}_z \left|\psi_{nlm}\right\rangle = \hbar m \left|\psi_{nlm}\right\rangle, \tag{3}$$

hence the energy levels are now:

$$E_{n,m} = \left\langle\psi_{nlm}\right| \hat{H} \left|\psi_{nlm}\right\rangle = \left\langle\psi_{nlm}\right| \hat{H}_0 \left|\psi_{nlm}\right\rangle + \frac{\mu_B}{\hbar}\left\langle\psi_{nlm}\right| \hat{L}_z \left|\psi_{nlm}\right\rangle B \tag{4}$$

$$= E_n + m\mu_B B = -\frac{(1Ry)}{n^2} + m\mu_B B, \tag{5}$$

where we have used that $\hat{H}_0 \left|\psi_{nlm}\right\rangle = E_n \left|\psi_{nlm}\right\rangle$, with E_n the eigenvalues of the unperturbed hydrogen Hamiltonian.

3. We recall that for a given orbital quantum number l, the magnetic quantum number m can take the following values: $-l, -l+1, ..., -1, 0, +1, ..., l-1, l$. Therefore, we can use Eq. (5), and list energies for the following orbitals: s ($l = 0$), p ($l = 1$), and d ($l = 2$).

The energies of s orbitals ($l = 0$) remain unaffected since $m = 0$:

$E_{n,0} = E_n$.

---

[1] In practice one cal also take $\mu \simeq m_e$ since $M_p >> m_e$.

Instead, p orbitals ($l = 1$, $m = -1, 0, 1$) split into three different levels:
$E_{n,-1} = E_n - \mu_B B$,
$E_{n,0} = E_n$,
$E_{n,1} = E_n + \mu_B B$.
Also, d orbitals ($l = 2$, $m = -2, -1, 0, 1, 2$) split into five different levels:
$E_{n,-2} = E_n - 2\mu_B B$,
$E_{n,-1} = E_n - \mu_B B$,
$E_{n,0} = E_n$,
$E_{n,1} = E_n + \mu_B B$,
$E_{n,2} = E_n + 2\mu_B B$.

Exercise 2: Auf-bau principle

a. Using the Auf-bau filling scheme we obtain that the electronic configuration for Li is $1s^2 2s^1$, i.e. two electrons in the $1s$ orbital and one electron in the $2s$ orbital.

b. Considering Li as a hydrogen-like atom, we can write the total energy (in Hartree units) as a sum of the energies of all the electrons in the system, namely:

$$E_{Li} = -\sum_{i=1}^{3} \frac{Z_{\mathrm{eff},i}^2}{2\, n_i^2}\,, \tag{6}$$

where $Z_{\mathrm{eff},i}$ is the effective charge felt by the i-th electron, and n_i is the principal quantum number of the i-th electron. The effective nuclear charge on an electron is given by $Z_{\mathrm{eff},i} = Z - S_i$ where Z is the number of protons in the nucleus (atomic number), and S_i is the number of electrons between the nucleus and the i-th electron (the number of non-valence electrons). Note that this is the approximate formula that neglects the dependence of E_{Li} on the quantum number l, induced by the dependence of $Z_{\mathrm{eff},i}$ on the distance from the nucleus. To be more quantitatively precise one should use $n_i^* = n_i - \delta_{n,l}$, where $\delta_{n,l}$ is an atom-dependent correction. Therefore, in the case of Li we have two $1s$ electrons (hence $n_1 = n_2 = 1$) which feel the charge $Z_{\mathrm{eff},1} = Z_{\mathrm{eff},2} = 3$, and one $2s$ electron (hence $n_3 = 2$) which feels the charge $Z_{\mathrm{eff},3} = 3 - 2 = 1$. Therefore, the total enegy of the system in Hartree atomic units is:

$$E_{Li} = -\frac{3^2}{2 \cdot 1^2} - \frac{3^2}{2 \cdot 1^2} - \frac{1^2}{2 \cdot 2^2} = -\frac{73}{8} = -9.125\,\mathrm{Ha}\,. \tag{7}$$

Exercise 3: Noble gas in a weak magnetic field

1. The electronic configuration of Ne is $1s^2 2s^2 2p^6$. Since all the electronic shells are fully occupied (it is a "closed shell" atom) the atom is particularly stable and chemically inert.

   Because of the absence of electron-electron interaction, every electron is subject to the same Coulombic potential and the accidental degeneracy in l you have seen for the hydrogen atom holds in this case as well due to the central nature of this potential. Therefore, based on the electronic structure, we have only two n energy levels occupied:

- $n = 1$ with 2 electrons on the s ($l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$, and $l = 0$, $m_l = 0$, $m_s = \frac{1}{2}$)
- $n = 2$ with 8 electrons, 2 on the s state $l = 0$ ($l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$, $m_s = \frac{1}{2}$) and 6 electrons on the p states $l = 1$ ($l = 1$, $m_l = -1, 0, +1$, $m_s = -\frac{1}{2},\frac{1}{2}$)

2. The total Hamiltonian describing the electrons of the Ne atom in a magnetic field is:

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_i} + \sum_i \frac{\mu_B}{\hbar}(\hat{L}_{z,i} + 2\hat{S}_{z,i})B_z,$$

where, in the independent particle picture, the operators $\hat{L}_{z,i}$ and $\hat{S}_{z,i}$ are meant to act only on the i-th electron.

3. Due to coupling with the external magnetic field the electronic energy levels E_n are modified as follows (remember that the eigenfunctions of the Hamiltonian can be chosen to be eigenfunctions of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$ and $\hat{S}_z$, because of the commutation of these operators with $\hat{H}$):

$$E_{nlm_lm_s} = E_n + \frac{\mu_B B_z}{\hbar}\langle\psi_{nlm_lm_s}|\hat{L}_z + 2\hat{S}_z|\psi_{nlm_lm_s}\rangle = E_n + \mu_B B_z(m_l + 2m_s).$$

Here are the final energies for all the electrons of the Ne atom:

- $1s$ electrons: $n = 1$, $l = 0$, $m_l = 0$
  - $m_s = \frac{1}{2}$: $E = E_1 + \mu_B B_z$
  - $m_s = -\frac{1}{2}$: $E = E_1 - \mu_B B_z$
- $2s$ electrons: $n = 2$, $l = 0$, $m_l = 0$
  - $m_s = \frac{1}{2}$: $E = E_2 + \mu_B B_z$
  - $m_s = -\frac{1}{2}$: $E = E_2 - \mu_B B_z$
- $2p$ electrons: $n = 2$, $l = 1$
  - $m_l = -1$
    - $m_s = \frac{1}{2}$: $E = E_2$
    - $m_s = -\frac{1}{2}$: $E = E_2 - 2\mu_B B_z$
  - $m_l = 0$
    - $m_s = \frac{1}{2}$: $E = E_2 + \mu_B B_z$
    - $m_s = -\frac{1}{2}$: $E = E_2 - \mu_B B_z$
  - $m_l = 1$
    - $m_s = \frac{1}{2}$: $E = E_2 + 2\mu_B B_z$
    - $m_s = -\frac{1}{2}$: $E = E_2$

As it is easy to realize by summing all these values, the total energy remains unchanged. This is a consequence of the fact that Ne has its shells complete. For the same reason the net magnetic moment that the system acquires under the effect of the magnetic field is 0.

4. Since $\hat{L}_x$ does not commute with $\hat{L}_z$, the corresponding component of the angular momentum is not conserved after the magnetic field is switched on ($[\hat{H}, \hat{L}_x] \neq 0$). The same conclusion holds for $\hat{S}_y$. Within a semi classical picture of the atom immersed in the magnetic field you can think of the angular (and spin) momenta as vectors precessing around the direction (z) of

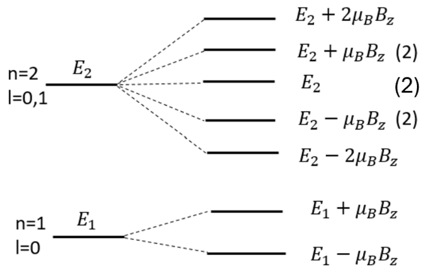

Figure 1: Schematic view of the energy levels. Note that some levels are degenerate.

the field so that only their z component and their projection onto the xy plane are conserved. In fact, $\hat{L}_x^2 + \hat{L}_y^2$ is conserved: you can see this by rewriting this operator as $\hat{L}^2 - \hat{L}_z^2$:

$$\langle \hat{L}_x^2 + \hat{L}_y^2 \rangle = \langle \hat{L}^2 - \hat{L}_z^2 \rangle = \langle \psi_{nlm_lm_s} | \hat{L}^2 - \hat{L}_z^2 | \psi_{nlm_lm_s} \rangle = \hbar^2 [l(l+1) - m_l^2].$$

Its eigenvalues $\hbar^2[l(l+1) - m_l^2]$ are conserved in time (constants of motion).

- s electrons:
  $l = 0$, $m_l = 0$, $\langle \hat{L}_x^2 + \hat{L}_y^2 \rangle = 0$
- p electrons:
  $l = 1$, $m_l = -1$, $\langle \hat{L}_x^2 + \hat{L}_y^2 \rangle = \hbar^2$
  $l = 1$, $m_l = 0$, $\langle \hat{L}_x^2 + \hat{L}_y^2 \rangle = 2\hbar^2$
  $l = 1$, $m_l = 1$, $\langle \hat{L}_x^2 + \hat{L}_y^2 \rangle = \hbar^2$