Multi-electron Atoms
Chapter 21

P. J. Grandinetti

Chem. 4300

Nov 20, 2017

The Helium Atom

As before we can, to good approximation, separate wave function into 2 parts: one for center of mass and other for 2 electrons orbiting center of mass. Hamiltonian for 2 electrons of He-atom is

$$\hat{H}_{\mathsf{He}} = \underbrace{-\frac{\hbar^2}{2m_e}\nabla_1^2}_{\hat{K}_H(1)} \underbrace{-\frac{\hbar^2}{2m_e}\nabla_2^2}_{\hat{K}_H(2)} \underbrace{-\frac{Zq_e^2}{4\pi\epsilon_0 r_1}}_{\hat{V}_H(1)} \underbrace{-\frac{Zq_e^2}{4\pi\epsilon_0 r_2}}_{\hat{V}_H(2)} + \underbrace{\frac{q_e^2}{4\pi\epsilon_0 r_{12}}}_{\hat{V}_{\mathsf{e\text{-}e}}}.$$

- 1st and 2nd terms on left, $\hat{K}_H(1)$ and $\hat{K}_H(2)$, are kinetic energies for 2 electrons
- 3rd and 4th terms, $\hat{V}_H(1)$ and $\hat{V}_H(2)$, are Coulomb attractive potential energy of each electron to nucleus
- 5th term inside brackets, $\hat{V}_{\mathsf{e\text{-}e}}$, is electron-electron Coulomb repulsive potential energy.
- It is electron-electron repulsive term that makes finding analytical solution more complicated.
- Repulsive term is not small perturbation when compared to other terms in Hamiltonian, so we cannot ignore it.

What happens if we ignore the e⁻–e⁻ repulsion term?

We have non-interacting electrons.

Consider solutions we get when repulsive term is removed

$$\hat{\mathcal{H}}_{\text{He}} = \hat{K}_H(1) + \hat{V}_H(1) + \hat{K}_H(2) + \hat{V}_H(2) = \hat{\mathcal{H}}_{\text{H}}(1) + \hat{\mathcal{H}}_{\text{H}}(2)$$

This $\hat{\mathcal{H}}_{\text{He}}$ is sum of 2 Hamiltonians each describing single e⁻ bound to He nucleus.

Orbital approximation is to express many electron wave function as product of one-electron wave functions:

$$\psi_{\text{He}} = \psi_H(1)\psi_H(2)$$

Thus, total energy is

$$E = -(1 \text{ Ry})\left(\frac{Z^2}{n_1^2} + \frac{Z^2}{n_2^2}\right)$$

For both electrons in $n_1 = n_2 = 1$ states of He atom obtain E = -108.86 eV

Measured ground state energy of He is -79.049 eV.

Thus, neglecting repulsion gives $\sim 38\%$ error in energy prediction.

The Variational Principle

The Variational Principle

Let's say you have a mathematical guess for ground state wave function.

Is there some way to determine if ψ_{guess} is a good guess?

Assume ψ_{guess} is well behaved and normalized wave function, and is some linear combination of exact eigenstates, ψ_n, of Hamiltonian, $\hat{\mathcal{H}}$,

$$\psi_{\text{guess}} = \sum_{n=0}^{\infty} c_n \psi_n$$

Exact eigenstates & coefficients, c_n, needed to describe ψ_{guess} are unknown.

Since ψ_{guess} is normalized, however, we know

$$\int_V \psi_{\text{guess}}^* \psi_{\text{guess}} d\tau = 1 = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} c_m^* c_n \int_V \psi_m^* \psi_n d\tau$$

Exact eigenstates are orthonormal, so $\int_V \psi_m^* \psi_n d\tau = 0$ when $m \neq n$.

Thus we know

$$\sum_{n=0}^{\infty} |c_n|^2 \int_V \psi_n^* \psi_n d\tau = \sum_{n=0}^{\infty} |c_n|^2 = 1$$

Each c_n is restricted to $|c_n| \leq 1$. If ψ_{guess} was perfect then

$$\psi_{\text{guess}} = \psi_0 \qquad \text{and} \quad c_0 = 1 \text{ while } c_{n \neq 0} = 0$$

The Variational Principle

Back to guess and calculate expansion

$$\int_V \psi_{\text{guess}}^* \hat{\mathcal{H}} \psi_{\text{guess}} d\tau = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} c_m^* c_n \int_V \psi_m^* \hat{\mathcal{H}} \psi_n d\tau$$

Again, ψ_n are exact eigenstates of $\hat{\mathcal{H}}$, so $\int_V \psi_m^* \hat{\mathcal{H}} \psi_n d\tau = 0$ when $m \neq n$.

$$\int_V \psi_{\text{guess}}^* \hat{\mathcal{H}} \psi_{\text{guess}} d\tau = \sum_{n=0}^{\infty} |c_n|^2 E_n \int_V \psi_n^* \psi_n d\tau = \sum_{n=0}^{\infty} |c_n|^2 E_n$$

Hope is that $\psi_{\text{guess}} \approx \psi_0$, with energy E_0. Rearranging

$$\int_V \psi_{\text{guess}}^* \hat{\mathcal{H}} \psi_{\text{guess}} d\tau = \sum_{n=0}^{\infty} |c_n|^2 \left(E_0 + (E_n - E_0) \right) = \sum_{n=0}^{\infty} |c_n|^2 E_0 + \sum_{n=0}^{\infty} |c_n|^2 (E_n - E_0)$$

$$= E_0 + \sum_{n=0}^{\infty} |c_n|^2 (E_n - E_0)$$

Since both $|c_n|^2$ and $(E_n - E_0)$ can only be positive numbers we obtain

$$\int_V \psi_{\text{guess}}^* \hat{\mathcal{H}} \psi_{\text{guess}} d\tau \geq E_0$$

The Variational Principle

This is called the *variational theorem*.

$$\int_V \psi^*_{\text{guess}} \hat{\mathcal{H}} \psi_{\text{guess}} d\tau \geq E_0$$

- It tells us that any variation in guess that gives lower expectation value for $\langle \hat{\mathcal{H}} \rangle$ brings us closer to correct ground state wave function and ground state energy.

- Suggests algorithm of varying some parameters, $a, b, c, \ldots$, in $\psi_{\text{guess}}(a, b, c, \ldots, \vec{x}_1, \vec{x}_2, \ldots)$ and searching for minimum in $\int_V \psi^*_{\text{guess}}(a, b, c, \ldots, \vec{x}_1, \vec{x}_2, \ldots) \hat{\mathcal{H}} \psi_{\text{guess}}(a, b, c, \ldots, \vec{x}_1, \vec{x}_2, \ldots) d\tau$ to get best guess for $\psi_{\text{guess}}(a_{\text{best}}, b_{\text{best}}, c_{\text{best}}, \ldots, \vec{x}_1, \vec{x}_2, \ldots)$.

Example

Apply variational principle to trial wave function for He atom making orbital approximation,

$$\psi_{\text{He}} = \psi_H(1)\,\psi_H(2)$$

using $\psi_H(1) = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z'}{a_0}\right)^{3/2} e^{-Z' r_1/a_0}$ and $\psi_H(2) = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z'}{a_0}\right)^{3/2} e^{-Z' r_2/a_0}$

and use Z' as variational parameter. Idea for replacing atomic number, Z, by Z' is that each electron sees smaller effective nuclear charge due to "screening" by other electron.

Solution: Recalling

$$\hat{\mathcal{H}}_{\text{He}} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Zq_e^2}{4\pi\epsilon_0 r_1} - \frac{Zq_e^2}{4\pi\epsilon_0 r_2} + \frac{q_e^2}{4\pi\epsilon_0 r_{12}}$$

Then,

$$\langle\hat{H}\rangle = \int \psi_H^*(1)\underbrace{\left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Zq_e^2}{4\pi\epsilon_0 r_1}\right]}_{\hat{H}_{\mathbf{H}}(1)}\psi_H(1)d\tau + \int \psi_H^*(2)\underbrace{\left[-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Zq_e^2}{4\pi\epsilon_0 r_2}\right]}_{\hat{H}_{\mathbf{H}}(2)}\psi_H(2)d\tau + \int \psi_H^*(1)\psi_H^*(2)\underbrace{\left[\frac{q_e^2}{4\pi\epsilon_0 r_{12}}\right]}_{\hat{V}_{\mathbf{e\text{-}e}}}\psi_H(1)\psi_H(2)d\tau$$

Example

Expand and rearrange 1st and 2nd terms taking $\Delta Z = Z - Z'$ (or $Z = \Delta Z + Z'$)

$$\langle \hat{\mathcal{H}} \rangle = \int \psi_H^*(1) \left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Z'q_e^2}{4\pi\epsilon_0 r_1} \right] \psi_H(1)d\tau - \int \psi_H^*(1)\frac{\Delta Z q_e^2}{4\pi\epsilon_0 r_1}\psi_H(1)d\tau$$

$$+ \int \psi_H^*(2) \left[-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Z'q_e^2}{4\pi\epsilon_0 r_2} \right] \psi_H(2)d\tau - \int \psi_H^*(2)\frac{\Delta Z q_e^2}{4\pi\epsilon_0 r_2}\psi_H(2)d\tau$$

$$+ \int \psi_H^*(1)\psi_H^*(2) \left[\frac{q_e^2}{4\pi\epsilon_0 r_{12}} \right] \psi_H(1)\psi_H(2)d\tau$$

1st and 3rd terms are H-atom energies except with Z'. We know these solutions. For 2nd and 4th terms we have

$$-\int \psi_H^*(1)\frac{\Delta Z q_e^2}{4\pi\epsilon_0 r}\psi_H(1)d\tau = -\frac{\Delta Z q_e^2}{4\pi\epsilon_0}\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 \int_0^\infty r^{-1}e^{-2Z'r/a_0}4\pi r^2 dr = -\frac{\Delta Z q_e^2}{4\pi\epsilon_0}\frac{Z'}{a_0}$$

5th term is more work and I'll leave it as an exercise to show that

$$\int \psi_H^*(1)\psi_H^*(2) \left[\frac{q_e^2}{4\pi\epsilon_0 r_{12}} \right] \psi_H(1)\psi_H(2)d\tau = \frac{5Z'q_e^2}{4\pi\epsilon_0}\frac{1}{8a_0}$$

Example

Bringing it all together gives

$$\langle \hat{\mathcal{H}} \rangle = 2 \left[-\frac{Z'^2 q_e^2}{8\pi\epsilon_0 a_0} \right] - 2 \left[\frac{Z' \Delta Z' q_e^2}{4\pi\epsilon_0 a_0} \right] + \frac{5Z' q_e^2}{4\pi\epsilon_0} \frac{1}{8a_0} = \left[Z'^2 - 2\left(Z - \frac{5}{16}\right) Z' \right] \frac{q_e^2}{4\pi\epsilon_0 a_0}$$

Now comes minimization step where we calculate $d\langle\hat{\mathcal{H}}\rangle/dZ' = 0$ as

$$\frac{d\langle\hat{\mathcal{H}}\rangle}{dZ'} = 2 \left[Z' - \left(Z - \frac{5}{16}\right) Z' \right] \frac{q_e^2}{4\pi\epsilon_0 a_0} = 0 \quad \text{which gives } \Delta Z = 5/16.$$

$$\text{Thus we find} \quad \langle\hat{\mathcal{H}}\rangle = -\left(Z - \frac{5}{16}\right)^2 \frac{q_e^2}{4\pi\epsilon_0 a_0} \geq E_0$$

For helium where $Z = 2$ we find $Z' = Z - \Delta Z = 2 - \frac{5}{16} = 1.6875$. We can think of this Z' value as effective charge of nucleus after screening by other electron. For ground state energy this leads to

$$\langle\hat{\mathcal{H}}\rangle = -\left(\frac{27}{16}\right)^2 \frac{q_e^2}{4\pi\epsilon_0 a_0} = -2.85 \frac{q_e^2}{4\pi\epsilon_0 a_0} = -77.5 \text{ eV},$$

a value that is in error by only 1.9%

Making the Orbital Approximation Good

The orbital approximation — the idea that electrons occupy individual orbitals — is not something chemists would give up easily.

In orbital approximation we write He atom ground state as

$$\psi = \frac{1}{\sqrt{2}}\psi_{1s}(1)\psi_{1s}(2)\left[\alpha(2)\beta(1) - \alpha(1)\beta(2)\right]$$

But now you know that electron–electron repulsion term spoils this picture, making it only an approximation.

Mean field potential energy

In 1927 Douglass Hartree proposed an approach for solving multi-electron Schrödinger Eq that makes orbital approximation reasonably good.

In Hartree's approach each single electron is presumed to move in combined potential field of

- nucleus, taken as point charge Zq_e, and
- all other electrons, taken as continuous negative charge distribution.

$$V_i(\vec{r}) \approx -\frac{Zq_e^2}{4\pi r} + \sum_{j=1, j\neq i}^{N} \frac{q_e^2}{4\pi\epsilon_0} \int_V \frac{\left|\psi_j(\vec{r})\right|^2}{\left|\vec{r} - \vec{r'}\right|} d^3\vec{r'}$$

$V_i(\vec{r})$ is "mean field" potential energy for ith electron in multi-electron atom.

Details of Hartree's approach and later refinements are quite complicated.

For now we use it to go forward with confidence with the orbital approximation.

Douglas Hartree with Mathematician Phyllis Nicolson at the Hartree Differential Analyser at Manchester University in 1935.

Making the Orbital Approximation Good

- Consequence of Hartree's successful solution is that chemists think of atoms and molecules in terms of single electrons moving in effective potential of nuclei and other electrons.

- For given electron of interest effective charge, Z_{eff}, seen by this electron is

$$Z_{\text{eff}} = Z - \sigma$$

  Z is full nuclear charge, and σ is shielding by average number of electrons between nucleus and ith electron.

- In multi-electron atom σ *increases with increasing* ℓ.

  ▶ This is because electrons in s orbital have greater probability of being near nucleus than p orbital, so electron of interest in s orbital sees greater fraction of nuclear charge than if it was a p orbital.

  ▶ Likewise when electron of interest is in p orbital it sees greater fraction of nuclear charge than if it was in d orbital.

Energy of ith electron varies with both n and ℓ
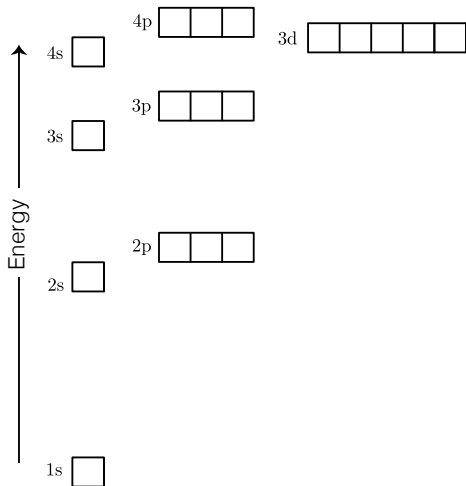
- Distinguish electrons with same n and ℓ value as being in same *subshell*.

- Ground state electron configuration is obtain by filling orbitals one electron at a time, in order of increasing energy starting with lowest energy.

- Electrons in outer most shell of atom are *valence electrons*, while electrons in inner closed shells are *core electrons*.

Periodic Trends and Table

- Before QM there were many attempts to arrange known elements so that there were some correlations between their known properties.

- in 1869 Dimitri Mendeleev made first reasonably successful attempt by arranging elements in order of increasing atomic mass, and, most importantly, found that elements with similar chemical and physical properties occurred periodically. He placed these similar elements under each other in columns.

- In 1914 Henry Moseley determined it was better to order elements by increasing atomic number, giving us periodic table we have today. Periodic table is arrangement of elements in order of increasing atomic number placing those with similar chemical and physical properties in columns.

- Vertical columns are called groups.

- Elements within a group have similar chemical and physical properties.

- Groups are designated by numbers 1-8 and by letters A and B at top.

- Horizontal rows are called periods, designated by numbers on left.

- Two rows placed just below main body of table are inner transition elements.

Atomic radii
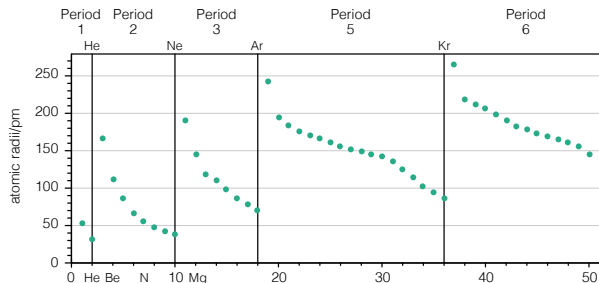
1. *Size generally decreases across period from left to right.* The more strongly attracted the outermost valence electron is to nucleus then smaller atom will be. Inner electrons in s orbitals shield nuclear charge better than those in p orbitals. Inner electrons in p orbitals shield nuclear charge better than those in d orbitals, and so forth. Across period ability of inner electrons to cancel increasing nuclear charge diminishes and outermost electron becomes more strongly attracted.

2. *Size increases down a group.* Increasing principal quantum number, n, of valence orbitals means larger orbitals and an increase in atom size.
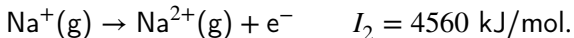
Ionization Energy

Amount of energy required to remove an e^- from gaseous atom or ion is called *ionization energy*.

First ionization energy, I_1, is energy required to remove highest energy e^- from neutral gaseous atom.

$$Na(g) \rightarrow Na^+(g) + e^- \qquad I_1 = 496 \text{ kJ/mol.}$$
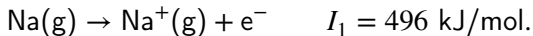
Ionization energy is positive because it requires energy to remove e^-.

Second ionization energy, I_2, is energy required to remove 2nd e^- from singly charged gaseous cation.

$$Na^+(g) \rightarrow Na^{2+}(g) + e^- \qquad I_2 = 4560 \text{ kJ/mol.}$$

Second ionization energy is almost 10 times that of 1st because number of e^-s causing repulsions is reduced.

Third ionization energy, I_3, is energy required to remove 3rd electron from doubly charged gaseous cation.

$$Na^{2+}(g) \rightarrow Na^{3+}(g) + e^- \qquad I_3 = 6913 \text{ kJ/mol.}$$
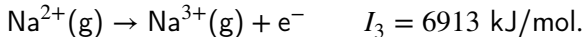
Ionization Energy

- 3rd ionization energy is even higher than 2nd.

- Successive ionization energies increase in magnitude because number of e⁻s, which cause repulsion, steadily decrease.

- Not a smooth curve. Big jump in ionization energy after atom has lost valence electrons.

- Atom that has same electronic configuration as noble gas is really going to hold on to its e⁻s.

- Amount of energy needed to remove e⁻s beyond valence electrons is significantly greater than energy of chemical reactions and bonding.

- Only valence electrons (i.e., e⁻s outside of noble gas core) are involved in chemical reactions.

1st ionization energy
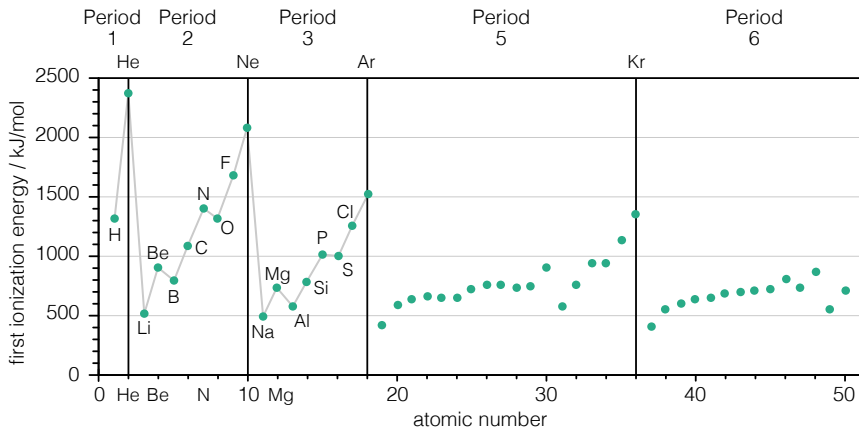
1st ionization energies generally increase as atomic radius decreases. Two clear behaviors are observed:

- *1st ionization energy increases across period.*
- *The first ionization energy decreases down a group.*

1st ionization energy

- *1st ionization energy increases across period.*
    - ▶ Because e^- in same principal quantum shell do not completely shield increasing nuclear charge of protons. e^-s are held more tightly and require more energy to be ionized.
      e.g., $I_1(\text{Cl}) > I_1(\text{Na})$ and $I_1(\text{S}) > I_1(\text{Mg})$.
    - ▶ Plot of ionization energy versus atomic number is not perfect line as there are easily explained exceptions to rules. Filled and half-filled subshells show small increase in stability in same way that filled shells show increased stability.
    - ▶ When trying to remove e^- from one of these filled or half-filled subshells, slightly higher ionization energy is found. e.g., $I_1(\text{Be}) > I_1(\text{B})$.
    - ▶ It is harder to ionize e^- from Be than B because Be has filled s sub-shell. e.g., $I_1(\text{N}) > I_1(\text{O})$. N has half-filled 2p sub-shell so it is harder to ionize e^- from N than O.

- *The first ionization energy decreases down a group.* Because highest energy e^-s are, on average, farther from nucleus. As principal quantum number increases, size of orbital increases and e^- is easier to remove.
  e.g., $I_1(\text{Na}) > I_1(\text{Cs})$ and $I_1(\text{Cl}) > I_1(\text{I})$.

Electron Affinity

Energy associated with addition of electron to gaseous atom is called *electron affinity*.

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta E = -E_{EA} = -349 \text{ kJ/mol.}$$

- Sign on energy change is negative because energy is usually released in this process.

- More negative ΔE corresponds to greater attraction for e^-.

- An unbound e^- has an ΔE of zero.

- Convention is to define e^- affinity energy, E_{EA}, as negative of energy released in reaction.

Electron Affinity
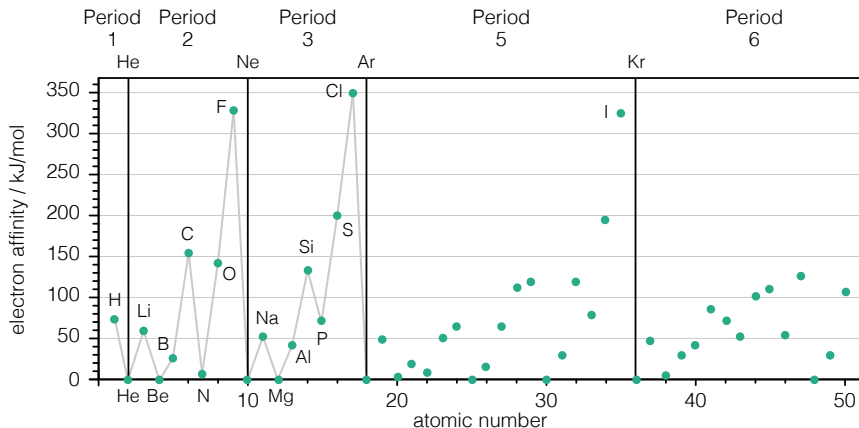
2 rules that govern periodic trends of e^- affinities:

1. e^- affinity becomes smaller down group.
2. e^- affinity decreases or increases across period depending on electronic configuration.

Electron Affinity

1. e^- affinity becomes smaller down group.

   ▶ As principal quantum number increases, size of orbital increases and affinity for e^- is less.

   ▶ Change is small and there are many exceptions.

2. e^- affinity decreases or increases across period depending on electronic configuration.

   ▶ This occurs because of same sub-shell rule that governs ionization energies.

   e.g., $E_{EA}(C) > E_{EA}(N)$.

   ▶ Since a half-filled p sub-shell is more stable, C has a greater affinity for an electron than N.

   ▶ Obviously, the halogens, which are one electron away from a noble gas electron configuration, have high affinities for electrons.

   ▶ F's electron affinity is smaller than Cl's because of higher electron–electron repulsions in smaller 2p orbital compared to larger 3p orbital of Cl.

Angular Momentum in Multi-electron Atoms

Angular Momentum in Atom with N electrons

In absence of external fields split $\hat{\mathcal{H}}$ for multi-electron atom into 3 parts:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{ee} + \hat{\mathcal{H}}_{SO}$$

$\hat{\mathcal{H}}_0$ is electron kinetic energy and nuclear Coulomb attraction:

$$\hat{\mathcal{H}}_0 = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Zq_e^2}{4\pi\epsilon_0 r_i} \right]$$

$\hat{\mathcal{H}}_{ee}$ is electron repulsion:

$$\hat{\mathcal{H}}_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{q_e^2}{4\pi\epsilon_0 r_{ij}}$$

$\hat{\mathcal{H}}_{SO}$ is spin-orbit coupling:

$$\hat{\mathcal{H}}_{SO} = \sum_{i=1}^{N} \xi(r_i)\vec{\ell}_i \cdot \vec{s}_i$$

There are additional interactions we could add to total $\hat{\mathcal{H}}$, but these can be handled later as perturbations to $\hat{\mathcal{H}}$.

Angular Momentum in Atom with N electrons

In absence of external fields split $\hat{\mathcal{H}}$ for multi-electron atom into 3 parts:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{ee} + \hat{\mathcal{H}}_{SO}$$

- In H-atom we saw that spin orbit coupling was small correction to $\hat{\mathcal{H}}_0$.

- In He-atom with 2 electrons we also find that $\hat{\mathcal{H}}_{SO}$ is small compare to $\hat{\mathcal{H}}_{ee}$.

- For multi-electron atoms with low number of electrons ($N < 40$) we can take $\hat{\mathcal{H}}_{SO}$ as small perturbation compared to $\hat{\mathcal{H}}_{ee}$, and take

$$\hat{\mathcal{H}}_I^{(0)} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{ee} \quad \text{for low } Z \text{ atoms.}$$

- On other hand, we know that $\hat{\mathcal{H}}_{SO}$ increases as Z^4. So when $N \gg 40$ we find that $\hat{\mathcal{H}}_{ee}$ is small perturbation compared to $\hat{\mathcal{H}}_{SO}$, and take

$$\hat{\mathcal{H}}_{II}^{(0)} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{SO} \quad \text{for high } Z \text{ atoms.}$$

Angular Momentum in Multi-electron Atom : Low Z case

In low Z case we find $\quad [\hat{\mathcal{H}}_I^{(0)}, \vec{\hat{L}}] = 0 \quad$ where $\quad \vec{L} = \sum_{i=1}^{N} \vec{\ell}_i$

$\vec{L}$ is total orbital angular momentum

$\vec{\ell}_i$ is individual electron orbital angular momentum.

In contrast to $\vec{\hat{L}}$ we find $\quad [\hat{\mathcal{H}}_I^{(0)}, \vec{\hat{\ell}}_i] \neq 0$.

Additionally, we can show $\quad [\hat{\mathcal{H}}_I^{(0)}, \vec{\hat{S}}] = 0 \quad$ where $\quad \vec{S} = \sum_{i=1}^{N} \vec{s}_i$.

$\vec{S}$ is total spin and $\vec{s}_i$ is individual e^- spin.

Since $\hat{\mathcal{H}}_I^{(0)}$ commutes with $\vec{\hat{L}}$ and $\vec{\hat{S}}$ then it must commute with $\vec{\hat{J}} = \vec{\hat{L}} + \vec{\hat{S}}$, that is,

$$[\hat{\mathcal{H}}_I^{(0)}, \vec{\hat{J}}] = 0.$$

In low Z limit we can approximate that individual orbital and spin angular momenta are separately conserved—since spin-orbit coupling is being neglected. This limit is called *Russell-Saunders coupling* or *LS coupling*.

Using L, S and J we label energy levels using atomic term symbols.

Angular Momentum : Low Z case, Hund's rules

If spin-orbit coupling is added back into Hamiltonian then degeneracy of different J levels is removed.

We can follow *Hund's rules* to determine which term corresponds to ground state:

1. Term with highest multiplicity, $(2S + 1)$, is lowest in energy. Term energy increases with decreasing multiplicity.

2. For terms with same multiplicity, $(2S + 1)$, term with highest L is lowest in energy.

3. If terms have same L and S, then for
   1. less than half-filled sub-shells the term with smallest J is lowest in energy.
   2. more than half-filled sub-shells the term with largest J is lowest in energy.

Angular Momentum : Low Z case, Hund's rules

Consider how terms are related to electron configuration in multi-electron atom.
Recall z components of $\vec{L}$ and $\vec{S}$ are given by sums

$$\hat{L}_z \psi = M_L \hbar \psi \text{ where } M_L = \sum_{i=1}^{N} m_{\ell,i} \quad \text{and} \quad \hat{S}_z \psi = M_S \hbar \psi \text{ where } M_S = \sum_{i=1}^{N} m_{s,i}$$

Example

What term symbol is associated with the $1s^2$ configuration?
Here we have

electron 1		electron 2		total	
m_ℓ	m_s	m_ℓ	m_s	M_L	M_S
0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0

Only one value of $M_L = 0$ in this configuration implying that $L = 0$.
Likewise, only one value of $M_S = 0$ implying that $S = 0$, (and $2S + 1 = 1$)
Since $J = L + S = 0$ has only one M_J value of $M_J = 0$.
$1s^2$ configuration belongs to term $^1S_0$ (pronounced "singlet S zero").

Example

What term symbol is associated with the $2p^6$ configuration?
Solution: From orbital diagram we see that both M_S and M_L sum to zero,

$$2\text{p} \quad \boxed{\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\downarrow} \quad \begin{array}{l} M_S = 0 \\ M_L = 0 \end{array}$$
$$\begin{array}{ccc} -1 & 0 & 1 \end{array}$$
$$m_\ell$$

Only $J = 0$ works so it belongs to $^1S_0$ term.
Note that we can ignore filled subshells.
We get same result when considering all subshells.

$$1\text{s} \boxed{\uparrow\downarrow} \quad 2\text{s} \boxed{\uparrow\downarrow} \quad 2\text{p} \boxed{\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\downarrow} \quad \begin{array}{l} M_S = 0 \\ M_L = 0 \end{array}$$
$$m_\ell = \quad 0 \qquad\qquad 0 \qquad\quad -1 \quad 0 \quad 1$$

All closed shells and subshells are $^1S_0$ terms.

Example

What are the terms associated with the $1s^1 2s^1$ configuration of helium?

Solution:. There are four possible states with $1s^1 2s^1$.

$$
\begin{array}{ccc}
 & 1s & 2s \\
m_\ell = & 0 & 0
\end{array}
$$

$$
\boxed{\uparrow} \quad \boxed{\uparrow} \quad M_S = 1, \; M_L = 0, \; M_J = 1
$$

$$
\boxed{\uparrow} \quad \boxed{\downarrow} \quad M_S = 0, \; M_L = 0, \; M_J = 0
$$

$$
\boxed{\downarrow} \quad \boxed{\uparrow} \quad M_S = 0, \; M_L = 0, \; M_J = 0
$$

$$
\boxed{\downarrow} \quad \boxed{\downarrow} \quad M_S = -1, \; M_L = 0, \; M_J = -1
$$

- All states have $M_L = 0$, so we must have $L = 0$.

- highest M_S value is $+1$ so need $S = 1$ which leads to $M_S = -1, 0, +1$.

- leaves 1 state with $M_S = 0$ and $M_L = 0$, must belong to $S = 0$, and $J = 0$.

- $1s^1 2s^1$ configuration leads to 2 terms:

  1. $^3S_1$ term for $L = 0$, $S = 1$, $J = 1$
  2. $^1S_0$ term for $L = 0$, $S = 0$, $J = 0$

Find terms for 2p^2 configuration of C? Which term is associated with ground state?

Solution: Number of ways to distribute n electrons to g spin orbitals in same sub-shell is
$\begin{pmatrix} G \\ N \end{pmatrix} = \frac{G!}{N!(G-N)!} = \frac{6!}{2!(6-2)!} = 15$ ways for 2p^2.

$m_\ell = -1$	0	1	M_L	M_S	M_J	Possible Terms
↑↓			-2	0	-2	¹D
↑	↑		-1	+1	0	³P
↑		↑	0	+1	+1	³P
	↑	↑	+1	+1	+2	³P
↑	↓		-1	0	-1	¹D,³P
↑		↓	0	0	0	¹D,³P,¹S
	↑↓		0	0	0	¹D,³P,¹S
	↑	↓	+1	0	+1	¹D,³P
↓	↑		-1	0	-1	¹D,³P
↓		↑	0	0	0	¹D,³P,¹S
	↓	↑	+1	0	+1	¹D,³P
↓	↓		-1	-1	-2	³P
↓		↓	0	-1	-1	³P
	↓	↓	+1	-1	0	³P
		↑↓	+2	0	+2	¹D

- Largest M_L magnitude is 2 with only $M_S = 0$. Must be $L = 2$, $S = 0$, $J = 2$, i.e., $^1D_2$, with 5 states have $M_L = -2, -1, 0, 1, 2$.

- With 5 states of $^1D_2$ eliminated next largest M_L magnitude remaining is 1 with M_S values of -1, 0, and $+1$. Must have $L = 1$, $S = 1$, $J = 0, 1, 2$, i.e., $^3P_0$, $^3P_1$, and $^3P_2$. Corresponds to 9 states.

- With 14 states of ^1D and ^3P eliminated, only 1 state left.
  Must be $S = 0$, $L = 0$, $J = 0$, i.e., $^1S_0$.

- To determine ground state term follow Hund's rule. Terms with highest multiplicity: $^3P_0$, $^3P_1$, and $^3P_2$. This sub-shell is less than half-filled, so term with lowest J, i.e., $^3P_0$, is ground state.

Angular Momentum in Multi-electron Atom : High Z case

$$\hat{\mathcal{H}}_{II}^{(0)} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{SO} \quad \text{for high } Z \text{ atoms.}$$

In high Z case we find $[\hat{\mathcal{H}}_{II}^{(0)}, \vec{\hat{L}}] \neq 0$ and $[\hat{\mathcal{H}}_{II}^{(0)}, \vec{\hat{S}}] \neq 0$ but $[\hat{\mathcal{H}}_{II}^{(0)}, \vec{\hat{j}}_i] = 0$ and

$$[\hat{\mathcal{H}}_{II}^{(0)}, \vec{\hat{J}}] = 0 \quad \text{where} \quad \vec{J} = \sum_{i=1}^{N} \vec{j}_i.$$

Here $j_i = \ell_i + s_i$.

In high Z limit individual orbital and spin angular momenta are not separately conserved.

This limit is called *j-j coupling*.

Term symbols for labeling energy levels do not work in this case.

Schrödinger Equation in Atomic Units

Schrödinger Equation in Atomic Units

Potential $\hat{V}(\vec{r})$ for electron bound to positively charged nucleus is given by coulomb potential

$$V(r) = \frac{-Zq_e^2}{4\pi\epsilon_0 r}$$

q_e is fundamental unit of charge and Z is nuclear charge in multiples of q_e.

3D Schrödinger equation for electron in hydrogen atom becomes

$$\left[-\frac{\hbar}{2\mu}\nabla^2 - \frac{Zq_e^2}{4\pi\epsilon_0 r} \right] \psi(\vec{r}) = E\psi(\vec{r})$$

In computational chemistry calculations it is easier to perform numerical calculations with all quantities expressed in atomic scale units to avoid computer roundoff errors.

Computational chemists go one step further and convert all distances in Schrödinger equation into dimensionless quantities by dividing by Bohr radius, $a_0 = 52.9177210526763$ pm

Schrödinger Equation in Atomic Units

Bohr radius is defined as *atomic unit of length*. A dimensionless distance vector is defined as

$$\vec{r'} \equiv \vec{r}/a_0$$

Laplacian in terms of dimensionless quantities becomes

$$\nabla'^2 = a_0^2 \nabla^2 = a_0^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = \frac{\partial^2}{\partial x^2} + \frac{\partial'^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2}$$

Converting wave function

$$|\psi(\vec{r})|^2 d\vec{r} = |\psi(\vec{r'})|^2 d\vec{r'} \text{ then } |\psi(\vec{r})|^2 = |\psi(\vec{r'})|^2 \frac{d\vec{r'}}{d\vec{r}} = \frac{1}{a_0} |\psi(\vec{r'})|^2$$

Then 1 electron Hamiltonian becomes

$$\left[-\frac{\hbar}{2\mu} \frac{1}{a_0^2} \nabla'^2 - \frac{Zq_e^2}{4\pi\epsilon_0 a_0 r'} \right] \frac{1}{\sqrt{a_0}} \psi(\vec{r'}) = E \frac{1}{\sqrt{a_0}} \psi(\vec{r'})$$

Schrödinger Equation in Atomic Units

With E_h as *atomic unit of energy*

$$E_h = \frac{\hbar^2}{m_e a_0^2} = \frac{q_e^2}{4\pi\epsilon_0 a_0}$$

and assumption that $\mu \approx m_e$ Schrödinger Eq becomes

$$E_h \left[-\frac{\nabla'^2}{2} - \frac{Z}{r'} \right] \psi(\vec{r'}) = E\psi(\vec{r'})$$

Dividing both sides by E_h and defining dimensionless energy $E' = E/E_h$ obtain

$$\left[-\frac{\nabla'^2}{2} - \frac{Z}{r'} \right] \psi(\vec{r'}) = E'\psi(\vec{r'})$$

Drop prime superscripts and write 1 e$^-$ atom dimensionless Schrödinger Eq as

$$\left[-\frac{\nabla^2}{2} - \frac{Z}{r} \right] \psi(\vec{r}) = E\psi(\vec{r})$$

Understood that all quantities are dimensionless and scaled by corresponding atomic unit quantity.

To obtain "dimensionful" quantities corresponding dimensionless quantity must be multiplied by corresponding atomic unit.

Values of selected atomic units in SI base units.

Quantity	Unit Symbol	Value in SI
length	a_0	$5.29177210526763 \times 10^{-11}$ m
mass	m_e	$9.10938356 \times 10^{-34}$ kg
charge	q_e	$1.6021766208 \times 10^{-19}$ C
energy	E_h	$4.359744651391459 \times 10^{-18}$ C
angular momentum	$\hbar$	$1.054571800139113 \times 10^{-34}$ J·s
electric dipole moment	$q_e a_0$	$8.478353549661393 \times 10^{-30}$ C·m
electric polarizability	$q_e^2 a_0^2 / E_h$	1.6488×10^{-41} C²·m²/J
electric field strength	$E_h/(q_e a_0)$	5.142206671012897 V/m
probability density	$1/(a_0^3)$	$6.748334508994266 \times 10^{-30}$ /m³

The Hamiltonian for a multi-electron atom in atomic units is given by

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \left[-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \right] + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{r_{ij}}.$$