One-electron system

The Hamiltonian

$$H_o \Psi_{total} = \left(\frac{p^2}{2\mu} - \frac{Z}{r} \right) \Psi_{total} = E\,\Psi_{total}$$

where the eigen function:

$$\Psi_{total} \equiv R_{n\ell}(r) Y_{\ell,m_\ell}(\theta,\varphi)\chi_{\pm}$$

has the uncoupled wave function representation $\left|\ell,m_\ell\right\rangle\left|s,m_s\right\rangle = \left|\ell,m_\ell,s,m_s\right\rangle$ which identify the orbital angular momentum, ℓ, and spin, s, parts of the wave function. m_ℓ is the projection quantum number associated with ℓ and m_s is the projection quantum number associated with s satisfies the relations:

$$\left\langle \ell',m'_\ell,s',m'_s \left| \hat{L}^2 \right| \ell,m_\ell,s,m_s \right\rangle = \ell(\ell+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m'_\ell}\delta_{m_s m'_s}$$

$$\left\langle \ell',m'_\ell,s',m'_s \left| \hat{L}_z \right| \ell,m_\ell,s,m_s \right\rangle = m_\ell\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m'_\ell}\delta_{m_s m'_s}$$

$$\left\langle \ell',m'_\ell,s',m'_s \left| \hat{S}^2 \right| \ell,m_\ell,s,m_s \right\rangle = s(s+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m'_\ell}\delta_{m_s m'_s}$$

$$\left\langle \ell',m'_\ell,s',m'_s \left| \hat{S}_z \right| \ell,m_\ell,s,m_s \right\rangle = m_s\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m'_\ell}\delta_{m_s m'_s}$$

Note: the quantum numbers $\left|\ell,m_\ell,s,m_s\right\rangle = \left|\ell,m_\ell\right\rangle\left|s,m_s\right\rangle$ diagonalize the Hamiltonian H_0 and they are called "good quantum numbers".

H.W. For the Hamiltonian H_0, examine the following relations:

$$\left[\hat{H}_o,\hat{L}^2\right] = \left[\hat{H}_o,\hat{S}^2\right] = \left[\hat{H}_o,\hat{L}_z\right] = \left[\hat{H}_o,\hat{S}_z\right] = 0$$

$$\left[\hat{S}^2,\hat{L}^2\right] = \left[\hat{L}_z,\hat{L}^2\right] = \left[\hat{L}^2,\hat{S}_z\right] = \left[\hat{L}_z,\hat{S}_z\right] = \left[\hat{S}^2,\hat{L}_z\right] = \left[\hat{S}^2,\hat{S}_z\right] = 0$$

Also, the wave function $\left|\ell,s,j,m_j\right\rangle$ in LSJ-coupling has similar relations:

$$\left\langle \ell',s',j',m'_j \left| \hat{L}^2 \right| \ell,s,j,m_j \right\rangle = \ell(\ell+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m'_j}$$

$$\left\langle \ell',s',j',m'_j \left| \hat{S}^2 \right| \ell,s,j,m_j \right\rangle = s(s+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m'_j}$$

$$\left\langle \ell',s',j',m'_j \left| \hat{J}^2 \right| \ell,s,j,m_j \right\rangle = j(j+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m'_j}$$

$$\left\langle \ell',s',j',m'_j \left| \hat{J}_z \right| \ell,s,j,m_j \right\rangle = m_j\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m'_j}$$

In which $\vec{J} = \vec{L} + \vec{S}$, and

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}.\hat{S} = \hat{L}^2 + \hat{S}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+,$$

Note that $\left|\ell,s,j,m_j\right\rangle$ are not eigenfunctions of $\hat{L}_z$ or $\hat{S}_z$. $\left|\ell,s,j,m_j\right\rangle$ are called "coupled representation".

H.W. For the Hamiltonian H_0, examine the following relations:

$$\left[\hat{L}^2,\hat{S}^2\right] = \left[\hat{L}^2,\hat{J}^2\right] = \left[\hat{L}^2,\hat{J}_z\right] = \left[\hat{S}^2,\hat{J}^2\right] = \left[\hat{S}^2,\hat{J}_z\right] = \left[\hat{J}^2,\hat{J}_z\right] = 0$$

$$\left[\hat{H}_o,\hat{L}^2\right] = \left[\hat{H}_o,\hat{S}^2\right] = \left[\hat{H}_o,\hat{J}^2\right] = \left[\hat{H}_o,\hat{J}_z\right] = 0$$

Collected formulae:

$$\hat{L}_y = (\hat{L}_+ - \hat{L}_-)/2i, \quad \hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2$$

$$\hat{L}_-\hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hat{L}_z, \quad \hat{L}_+\hat{L}_- = \hat{L}^2 - \hat{L}_z^2 + \hat{L}_z$$

$$\hat{L}_\pm |l,m\rangle = \sqrt{l(l+1) - m(m\pm 1)}\,|l,m\pm 1\rangle$$

$$\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y = \pm e^{\pm i\varphi}\left[\frac{\partial}{\partial\theta} \pm i\,\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$\hat{L}_z = -i\,\frac{\partial}{\partial\phi}, \quad \hat{L}^2 = -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$$

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}.\hat{S} = \hat{L}^2 + \hat{S}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+$$

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hat{J}_z, \quad \left[\hat{J}_y, \hat{J}_z\right] = i\hat{J}_x, \quad \left[\hat{J}_z, \hat{J}_x\right] = i\hat{J}_y \Rightarrow \vec{\hat{J}} \times \vec{\hat{J}} = i\vec{\hat{J}}$$

$$\hat{J}^2 \,|\, j, m_j > = j(j+1) \,|\, j, m_j >$$

$$\hat{J}_z \,|\, j, m_j > = m_j \,|\, j, m_j >; \quad \hat{J}_z^2 \,|\, j, m_j > = m_j^2 \,|\, j, m_j >$$

$$\hat{J}_\pm \,|\, j, m_j > = \sqrt{j(j+1) - m_j(m_j \pm 1)}\ \,|\, j, m_j \pm 1 >$$

$$\left[\hat{J}_+, \hat{J}_-\right] = 2\hat{J}_z, \quad \left[\hat{J}_z, \hat{J}_-\right] = -\hat{J}_-, \quad \left[\hat{J}_z, \hat{J}_+\right] = \hat{J}_+$$

$$\left[\hat{J}^2, \hat{J}_+\right] = \left[\hat{J}^2, \hat{J}_-\right] = \left[\hat{J}^2, \hat{J}_x\right] = \left[\hat{J}^2, \hat{J}_y\right] = \left[\hat{J}^2, \hat{J}_z\right] = 0,$$

H.W. For the following Hamiltonian:

$$H = H_0 + H_{SO} = -\frac{\nabla^2}{2m} - \frac{Z}{r} + \zeta(r)\ \vec{\mathrm{L}}\cdot\vec{\mathrm{S}}, \qquad \zeta(r) = \frac{Z\hbar^2 e^2}{2m^2c^2}\frac{1}{r^3},$$

Examine the following relations:

$$\left[\hat{S}^2, \hat{L}^2\right] = \left[\hat{L}_z, \hat{L}^2\right] = \left[\hat{L}^2, \hat{S}_z\right] = \left[\hat{L}_z, \hat{S}_z\right] = \left[\hat{S}^2, \hat{L}_z\right] = \left[\hat{S}^2, \hat{S}_z\right] = 0$$

$$\left[\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}, L^2\right] = \left[\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}, S^2\right] = \left[\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}, J^2\right] = \left[\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}, J_z\right] = 0$$

But $\left[\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}, L_z\right] \neq 0, \quad \left[\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}, S_z\right] \neq 0$

Conclusions:

1- For one or n-electrons system, both uncouple representation $\left|\ell_i, m_{\ell i}, s_i, m_{si}\right\rangle = \left|\ell_i, m_{\ell i}\right\rangle\left|s_i, m_{si}\right\rangle$ and the coupled representation $\left|\ell, s, j, m_j\right\rangle$ are eigenfunctions of H_o and it is immaterial which representation is used.

2- $\left|\ell, m_\ell, s, m_s\right\rangle$ will not necessarily be an eigenfunctions of $\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}$.

3- $\left|L, S, J, m_J\right\rangle$ is a simultaneous eigenfunctions of $\hat{J}^2$, $\hat{L}^2$, $\hat{S}^2$ and $\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}$.

Atomic Term Symbols

Assigning Term Symbols: The ground state of hydrogen atom is one electron in the lowest energy atomic orbital: the 1s. Therefore the total orbital angular momentum off all (one) electrons is:

$L = \ell = 0$, and the total electron spin is $S = s = \frac{1}{2}$.

The orbital angular momentum is given as letter symbol. J is the vector sum of L and S:

$$|\vec{J}| = L+S, L+S-1, L+S-2, \ldots, |L-S|$$

So, for 1s-state we have $J = 1/2$.

Example For p-electron we have $\ell = 1$, then the allowed values of $\vec{j}$ for a p-electron are:

$$\vec{j} = \vec{\ell} + \vec{s} = 1 + \frac{1}{2} = \frac{3}{2}$$

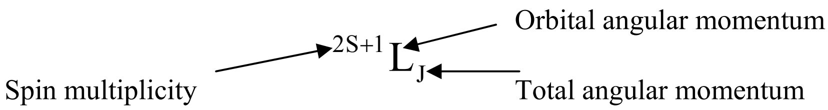
$$\vec{j} = \vec{\ell} - \vec{s} = 1 - \frac{1}{2} = \frac{1}{2}$$

Example: For a d-electron ($L = 2, \quad S = 1/2 \;\Rightarrow\; J = 5/2, 3/2$).

Comments: The Spin-Orbit Coupling Schemes (LSJ) (*Russell-Saunders Coupling*) is used for light atoms (Z is small, $Z < \approx 36$) and in the case of the Spin-orbit couplings of individual electrons are weak.

Applying the term symbol has the following information:

1.) Multiplicity
2.) Total angular momentum, $\vec{J}$
3.) Total orbital angular momentum, $\vec{L}$



The orbital angular momentum is given as letter symbol.

L	0	1	2	3	4	5	etc…
Symbol	S	P	D	F	G	H	etc…

Consequently, the atomic term symbol for the ground state of H-atom will be $^2S_{1/2}$. For the excited np-state, we have $^2P_{1/2}$ and $^2P_{3/2}$. For the nd-state we will have $^2D_{3/2}$ and $^2D_{5/2}$.

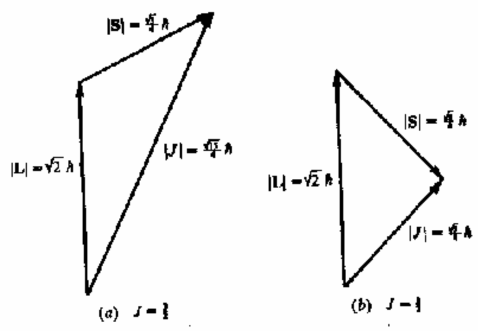
Example: Calculate the possible values of $\vec{L}\cdot\vec{S}$ for a p-electron $\left(\ell = 1, s = \frac{1}{2}\right)$.

Answer: Use the relation:

$$\vec{J} = \vec{L} + \vec{S} \quad\Rightarrow\quad |\vec{J}|^2 = (\vec{L}+\vec{S})^2 = |\vec{L}|^2 + |\vec{S}|^2 + 2\vec{L}\cdot\vec{S}$$

$$\therefore \vec{L}\cdot\vec{S} = \frac{1}{2}\left[|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2\right] = \frac{1}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

For $J = \frac{3}{2}$



The following figure illustrates the relative orientation of the three vectors.

$$\vec{L}\cdot\vec{S}=\frac{1}{2}\left[\frac{3}{2}(\frac{3}{2}+1)-1(1+1)-\frac{1}{2}(\frac{1}{2}+1)\right]=\frac{1}{2}$$

For $J=\frac{1}{2}$

$$\vec{L}\cdot\vec{S}=\frac{1}{2}\left[\frac{1}{2}(\frac{1}{2}+1)-1(1+1)-\frac{1}{2}(\frac{1}{2}+1)\right]=-1$$

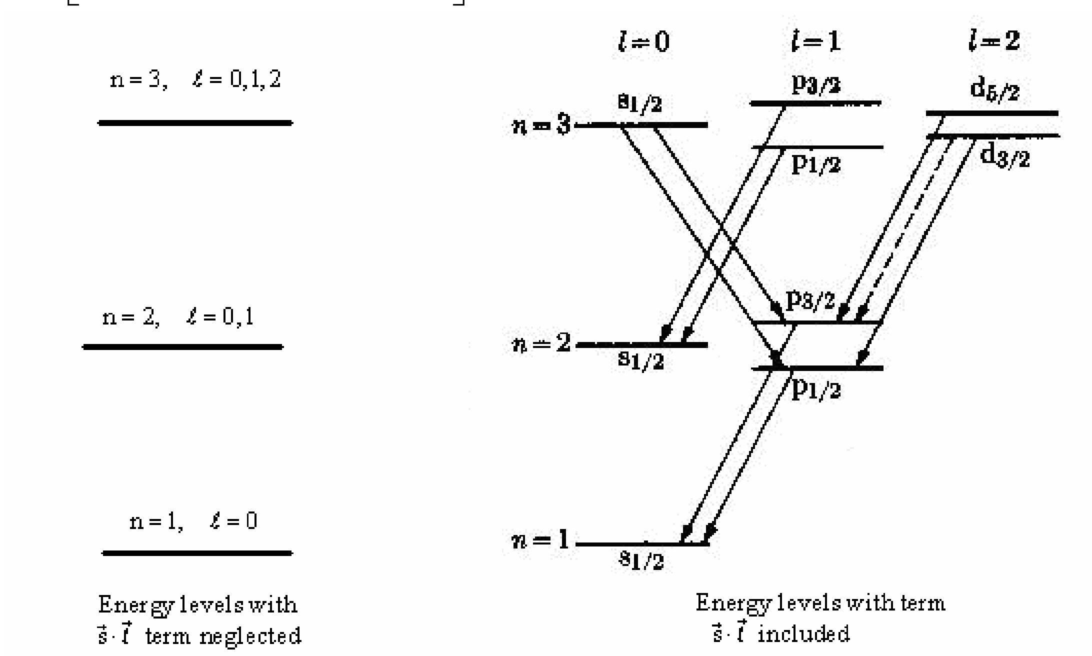


Figure: Spin-orbit splitting of energy levels and possible transitions.
The spin-orbit interaction splits each of the $\ell \neq 0$ states.

Notes:

1- The dashed line indicates a transition with very low probability.
2- The transition $3p \rightarrow 1s$ will be allowed but with low intensity compared with the transition $3p \rightarrow 2s$;

Example

Calculate $\mathbf{L}\cdot\mathbf{S}$ for a $^3F_2$ state.

For a $^3F_2$ state, $S = 1$, $L = 3$ and $J = 2$. From the result of Problem 22.1 we have

$$\mathbf{L}\cdot\mathbf{S}=\frac{1}{2}[J(J+1)-L(L+1)-S(S+1)]\hbar^2=\frac{1}{2}[2(2+1)-3(3+1)-1(1+1)]\hbar^2=-4\hbar^2$$

General recipe for working out the coupling states for N-electron

Going from the uncoupled states $|L,S,M_L,M_S\rangle$ to the coupled one $|L,S,J,M_J\rangle$, we have to do the following:

1- Calculate the allowed values of the total angular momentum J, i.e.

$$J=\underbrace{L+S}_{\text{1st-group}},\underbrace{L+S-1}_{\text{2nd-group}},L+S-2,\cdots,\underbrace{|L-S|}_{\text{last-group}}$$

where:

$$M_L = L, L-1, L-2, \cdots, -(L-1), -L;$$
$$M_S = S, S-1, S-2, \cdots, -(S-1), -S;$$
$$M_J = M_L + M_S$$
$$M_J = J, J-1, J-2, \cdots, -(J-1), -J$$

2- Identify the highest state with the maximum quantum number; in coupled i.e. $\left|J_{max} = L + S, M_{J_{max}} = M_{L_{max}} + M_{S_{max}}\right\rangle$ and the corresponding values in the uncoupled representation, i.e. $\left|L_{max}, S_{max}, M_{L_{max}}, M_{S_{max}}\right\rangle \equiv \left|M_{L_{max}}, M_{S_{max}}\right\rangle$.
3- Use the lower operators, for both representations, to calculate the following lower state.
4- Repeat step 3 till you reach the lowest state in the first group.
5- Go for second group and repeat steps 2-4 with orthogonality condition.
6- Repeat the process to reach the last group.

Atomic Units

They are obtained by defining $\hbar = 1, m_e = 1, e = 1, k = 1/4\pi\varepsilon_o = 1$ (a.u) (The units in the electron's world.) Note that in equating $\hbar = 1, m_e = 1, e = 1, k = 1/4\pi\varepsilon_o = 1$ the dimensions of these quantities are ignored. Hence, equations written in atomic units are not dimensionally correct in the usual sense.

The atomic unit of length, 1 Bohr, equals the radius of the lowest Bohr orbit in the hydrogen atom. In SI units,

$$a_o = \frac{\hbar^2}{kme^2} \approx 0.05 \text{ nm}.$$
$$a_o = \frac{\hbar^2}{kme^2} = 1 \quad \text{(atomic units)}$$

The atomic unit of energy, 1 Hartree, is defined to be twice the ionization energy of the hydrogen atom ($= -E_{pot}$ for the electron in the lowest Bohr orbit with n = 1). In SI units,

$$E_{pot} = \frac{ke^4}{a_o \hbar^2 n^2} \approx 27.2 \text{ eV}, \qquad n = 1$$
$$E = \frac{ke^4}{a_o} = 1 \quad \text{(atomic units)}$$

$$1 \text{ Hartree} = \frac{k^2 me^4}{\hbar^2} = \frac{me^4}{(4\pi\varepsilon_o)^2 \hbar^2} = \frac{(9.1091\text{x}10^{-31}\text{kg})(1.6021\text{x}10^{-19}\text{C})^4}{(1.1126\text{x}10^{-10}\text{C}^2.\text{J}^{-1}.\text{m}^{-1})^2(1.0545\text{x}10^{-34}\text{J.s})^2} = 4.3595\times10^{-18}\text{J}$$

$$1 \text{ Hartree (1 H)} = 4.3595\times10^{-18}\text{J} = 27.2 \text{ eV} = 2 \text{ Ry}$$

$$1 \text{ Hartree} = 2625 \text{ kJmol}^{-1}$$

Use $E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$, then

$$\bar{\nu} = \frac{1 \text{ Hartree}}{hc} = \frac{4.36\times10^{-18}\text{J}}{(6.626\times10^{-34}\text{J.s})(3.0\times10^8\text{m/s})} = 2.195\times10^7\text{m}^{-1} = 2.195\times10^5\text{cm}^{-1}$$

For hydrogen atom:

$$1\ \text{Ryd} = \frac{k^2 m e^4}{2\hbar^2} = \frac{m e^4}{2(4\pi\varepsilon_o)^2\hbar^2} = \frac{(9.1091\text{x}10^{-31}\text{kg})(1.6021\text{x}10^{-19}\text{C})^4}{2(1.1126\text{x}10^{-10}\text{C}^2.\text{J}^{-1}.\text{m}^{-1})^2(1.0545\text{x}10^{-34}\text{J.s})^2} = \frac{4.3595\times10^{-18}}{2}\text{J}$$

$$= 13.6\ \text{eV}$$

It could be written as:

$$1\ \text{Ryd} = \frac{1}{2}mc^2\left(\frac{k^2e^2}{\hbar c}\right)^2 = \frac{1}{2}mc^2\alpha^2,$$

where α is the fine-structure constant, $\alpha = \frac{1}{137}$ and $mc^2 = 511\ \text{keV}$. Then

$$\text{E}_\text{n}^{(0)} = -\frac{1}{n^2}\frac{k^2me^4}{2\hbar^2} = -\frac{1}{n^2}\frac{1}{2}mc^2\alpha^2$$

Note that:

$$\text{E}_1^{(0)} = -\frac{1}{2}mc^2\alpha^2 = -\frac{1}{2}\left(511\times10^3\ \text{eV}\right)\left(\frac{1}{137}\right)^2 = -13.6\ \text{eV}$$

Table: Conversion factor

1 Å (angström) = 0.1 nm = 10^{-10} m = 10^{-8} cm

1 fm (femtometer or Fermi) = 10^{-6} nm = 10^{-15} m

λ (in Å) × $\tilde{\nu}$ (in cm^{-1}) = 10^{8} (from $\lambda\tilde{\nu} = 1$)

$a_0 = 5.29177 \times 10^{-11}$ m = 0.529177 Å

$a_0^2 = 2.80028 \times 10^{-21}$ m^2

$\pi a_0^2 = 8.79735 \times 10^{-21}$ m^2

1 Hz = 1 s^{-1}

1 electron mass (m_e) = 0.511003 MeV/c^2

1 proton mass (M_p) = 938.280 MeV/c^2

1 a.m.u. = 1/12 $M_{^{12}C}$ = 1.66057×10^{-27} kg = 931.502 MeV/c^2

1 J = 10^7 erg = 0.239 cal = 6.24146×10^{18} eV

1 cal = 4.184 J = 2.611×10^{19} eV

1 eV = 1.60219×10^{-19} J = 1.60219×10^{-12} erg

1 MeV = 1.60219×10^{-13} J = 1.60219×10^{-6} erg

1 eV corresponds to:
- a frequency of 2.41797×10^{14} Hz (from $E = h\nu$)
- a wavelength of 1.23985×10^{-6} m = 12398.5 Å (from $E = hc/\lambda$)
- a wave number of 8.06548×10^{5} m^{-1} = 8065.48 cm^{-1} (from $E = hc\tilde{\nu}$)
- a temperature of 1.16045×10^{4} K (from $E = kT$)

1 cm^{-1} corresponds to
- an energy of 1.23985×10^{-4} eV
- a frequency of 2.99792×10^{10} Hz

1 atomic unit of energy = 27.2116 eV corresponds to
- a frequency of 6.57968×10^{15} Hz
- a wavelength of 4.55633×10^{-8} m = 455.633 Å
- a wave number of 2.19475×10^{7} m^{-1} = 219475 cm^{-1}
- a temperature of 3.15777×10^{5} K

1 a.m.u. corresponds to an energy of 931.502 MeV = 1.49244×10^{-10} J

$kT = 8.61735 \times 10^{-5}$ eV at $T = 1$ K

$hc = 1.23985 \times 10^{-6}$ eV × m = 12398.5 eV × Å

$\hbar c = 1.97329 \times 10^{-7}$ eV × m = 1973.29 eV × Å

ΔE (in eV) × Δt (in s) = 6.58218×10^{-16} eV × s (from $\Delta E \Delta t = \hbar$)