**ATOMS**

- Central field model (4 quantum numbers + Pauli exclusion)
  \[ n = 1, 2, 3, \ldots \]
  \[ 0 \leq l \leq n - 1 \quad (0, 1, 2, 3 \equiv s, p, d, f) \]
  \[ |m_l| \leq l, \quad m_s = \pm 1/2 \]

- Spectroscopic notation: \( ^{2S+1}L_J \) \((Z \leq 40)\)
  \( L \) is total orbital angular momentum \((0, 1, 2, 3 \equiv S, P, D, F)\)
  \( S \) is total spin angular momentum
  \( J = L + S; \quad (|L - S|, \ldots, L + S) \)
  \( \mathcal{E} = \mathcal{E}(L, S, J); \quad 2J + 1 \) states
  Weak dependence of \( \mathcal{E} \) on \( J \) (“fine structure”)

- Electronic configurations
  Hydrogen: \( 1s \quad (^2S_{1/2}) \)
  Oxygen: \( 1s^22s^22p^4 \quad (^3P_2) \)
  Argon: \( 1s^22s^22p^63s^23p^6 \quad (^1S_0) \)
  Metastable argon: \( 1s^22s^22p^63s^23p^54s \quad (^3P_0, \quad ^3P_2) \)
Atomic energy levels for the central field model of an atom, showing the dependence of the energy levels on the quantum numbers $n$ and $l$; the energy levels are shown for sodium, without the fine structure.
METASTABLE STATES

- Most excited states can radiate a photon and make a transition to a lower energy state
  \[ \implies \text{electric dipole radiation} \]

- **Selection rules** for electric dipole radiation
  - For all elements: \( \Delta l = \pm 1; \Delta J = 0, \pm 1 \)
    (but \( J = 0 \rightarrow J = 0 \) is forbidden)
  - For light elements: \( \Delta S = 0; \Delta L = 0, \pm 1 \)
    (but \( L = 0 \rightarrow L = 0 \) is forbidden)

- **Radiation lifetime** \( \tau_{\text{rad}} \sim 10^{-100} \text{ ns} \)

- Electric dipole radiation forbidden
  \[ \implies \text{metastable state} \]

- **Examples**: \( \text{Ar}(4s\,^3P_0), \text{Ar}(4s\,^3P_2) \)
ARGON ENERGY LEVELS

$2P_{1/2}$ (Ar$^+$) ionization limit

$2P_{3/2}$ (Ar$^+$) ionization limit

Energy (volts)

Ground state ($l=1$)

Ground state ($l=0$)

$3p^6$ ($-15.76$ V)

$1S_0$ ($-2.280$)
$3P_1$ ($-2.432$)
$3P_2$ ($-2.457$)
$1P_1$ ($-2.477$)
$1D_2$ ($-2.588$)
$3P_0$ ($-2.487$)
$1D_1$ ($-2.607$)
$3D_2$ ($-2.665$)
$3D_3$ ($-2.684$)
$3S_1$ ($-2.853$)

$1P_1$ ($-3.932$)
$3P_0$ ($-4.037$)
$3P_1$ ($-4.136$)
$3P_2$ ($-4.211$)

$1S_0$ ($-15.76$)

750.4 nm

104.9 nm

106.7 nm

LiebermanShortCourse08
- Electronic state is a function of nuclear separations
- Potential energy curves of electronic states of a diatomic molecule
- Attractive (1, 2) and repulsive (3) states
- Vibrations and rotations also quantized

\[ e\mathcal{E}_v = \hbar \omega_{vib} \left( v + \frac{1}{2} \right), \]
\[ v = 0, 1, 2, \ldots \]
• Notation for diatomic molecules: $^{2S+1} \Lambda$
  $\Lambda =$ total orbital angular momentum about internuclear axis
  $(0, 1, 2, 3, \equiv \Sigma, \Pi, \Delta, \Phi)$
  $S =$ total spin angular momentum

• For $\Sigma$ states, $\Sigma^+$ and $\Sigma^-$ denote symmetric or antisymmetric wave function with respect to reflection through internuclear axis

• For homonuclear molecules, $\Lambda_g$ and $\Lambda_u$ denote symmetric or antisymmetric wave function with respect to interchange of the nuclei
  (the two nuclei are the same; e.g., $O_2$, $N_2$, but not NO)
• Most excited molecular states can radiate a photon and make a transition to a lower energy state

\[ \implies \text{electric dipole radiation} \]

• Selection rules for electric dipole radiation

\[ \Delta \Lambda = 0, \pm 1 \]
\[ \Delta S = 0 \]

\[ \Sigma^+ \rightarrow \Sigma^+ \text{ and } \Sigma^- \rightarrow \Sigma^- \]
\[ g \rightarrow u \text{ and } u \rightarrow g \]

• Radiation lifetime \( \tau_{\text{rad}} \sim 10^{-10} \text{ ns} \)

• Electric dipole radiation forbidden \( \Rightarrow \) metastable state

• Examples are: \( \text{O}_2(a^1\Delta_g) \), \( \text{O}_2(b^1\Sigma_g^+) \)
• The energy required to remove the electron from a negative ion \((A^-)\) is called the **affinity energy** \(\mathcal{E}_{\text{aff}}\) of the neutral atom or molecule \(A\).

• Negative atomic and molecular ions \((A^-)\) are stable if \(\mathcal{E}_{\text{aff}} > 0\). Typically \(\mathcal{E}_{\text{aff}} \sim 0.5\text{–}3.5\) V for stable negative ions.

• Examples of stable negative ions are: \(H^-\) (but not \(H_2^-\)), \(O_2^-\), \(O^-\), \(Cl_2^-\), \(Cl^-\), \(F_2^-\), \(F^-\).

• Stable \(Ar^-\), \(N^-\), \(N_2^-\), \(H_2^-\) negative ions **do not exist**.

• Gas mixtures containing oxygen, hydrogen and/or the halogens are generally “attaching” or “electronegative” (stable negative ions can form).

• Nitrogen and the noble gases are “**electropositive**”.
C O L L I S I O N  P R I N C I P L E S

• Two kinds of collisions
  — Electron collisions with atoms and molecules
    \[ e + A \rightarrow \text{products} \]
  — Heavy particle collisions with atoms and molecules
    \[ A + B \rightarrow \text{products} \]
    \[ A^+ + B \rightarrow \text{products} \]
    \[ A^- + B \rightarrow \text{products} \]

• By Newton’s laws, two bodies cannot elastically collide to form one body
  \[ e + A \rightarrow A^- \]
  \[ A + B \rightarrow AB \]

• Two bodies can collide to form one body if the internal energy increases
  \[ e + A \rightarrow A^-* \]
  \[ A + B \rightarrow AB* \]
ELECTRON COLLISIONS WITH MOLECULES

- Frank-Condon principle
  Nuclear positions are fixed during an electronic transition
- Due to the ordering of timescales for an electron collision
  \[ \frac{2a_0}{v_e} \ll \tau_{\text{vib}} \sim \tau_{\text{diss}} \ll \tau_{\text{rad}} \]
  interac. time
  \[ a_0 = \text{radius of atom or molecule}; \ v_e = \text{speed of incoming electron} \]
- Dissociation
  \[ e + AB \rightarrow A + B + e \]
- Excitation
  \[ e + AB \rightarrow AB^* + e \]
- Ionization
  \[ e + AB \rightarrow AB^+ + 2e \]
EXAMPLE OF HYDROGEN

- Electronic transitions are vertical
- $8.8 \text{ V}: \; ^3\Sigma_u^+ \rightarrow \text{dissociation (2.2 V per atom)}$
- $11.5 \text{ V}: \; ^1\Sigma_u^+ \rightarrow \text{uv radiation}$
- $11.8 \text{ V}: \; ^3\Sigma_g^+ \rightarrow \text{radiation to } ^3\Sigma_u^+ \rightarrow \text{dissociation}$
- $12.6 \text{ V}: \; ^1\Pi_u \rightarrow \text{uv radiation}$
- $15.4 \text{ V}: \; ^2\Sigma_g^+ \rightarrow \text{H}_2^+ \text{ ions}$
- $28.0 \text{ V}: \; ^2\Sigma_u^+ \rightarrow \text{H} + \text{H}^+$ (5 V per fragment)
NEGATIVE ION PRODUCTION

- Dissociative attachment
  \[ e + O_2 \rightarrow O_2^- \text{(unstable)} \rightarrow e + O_2 \quad (99\%) \]
  \[ \rightarrow O + O^- \quad (1\%) \]

  Resonant process (no outgoing electron to carry away excess energy)
  Small probability process (small cross section, but important)
NEGATIVE ION PRODUCTION (CONT’D)

- **Dissociative attachment**
  \[ e + O_2 \rightarrow O^- \text{(unstable)} \rightarrow e + O_2 \quad (99\%) \]
  \[ \rightarrow O + O^- \quad (1\%) \]

- **Polar dissociation**
  \[ e + O_2 \rightarrow O^+ + O^- + e \]
  Non-resonant, high threshold energy
VIBRATIONAL AND ROTATIONAL EXCITATIONS

- Mechanism is often
  \[ e + AB(v = 0) \rightarrow AB^- \text{ (unstable)} \]
  \[ AB^- \rightarrow AB(v > 0) + e \]

ELECTRON COLLISIONAL ENERGY LOSSES

- Ionization
  Electronic excitation
  Elastic scattering
  Dissociation
  Vibrational excitation
  Rotational excitation
  etc.

- Electron collisional energy lost per electron-ion pair created, \( \mathcal{E}_c \), is 2–10 times larger for molecules than for atoms [p. 42]
HEAVY PARTICLE COLLISIONS

- Ordering of timescales [p. 158]
  \[
  \frac{2a_0}{v_e} \ll \frac{2a_0}{v_i} \sim \tau_{\text{vib}} \ll \tau_{\text{rad}}
  \]
  \( v_i = \) speed of incoming ion or neutral

- Adiabatic Massey principle
  Potential energy curves must cross or nearly touch for a change of electronic state (\( \Delta \mathcal{E} \lesssim 0.1 \text{ V} \))

- Examples
  \( A + B \rightarrow A^+ + B + e \) heavy particle ionization (very small)
  \( \text{(AB and AB}^+ \text{ curves do not cross or nearly touch)} \)
  \( A + B \rightarrow A^* + B \) heavy particle excitation (very small)
  \( A^+ + B \rightarrow A^+ + B \) elastic scattering (large)
  \( A^+ + A \rightarrow A + A^+ \) resonant charge transfer (large)
NONRESONANT CHARGE TRANSFER

- Example of nitrogen and oxygen atoms
  \[ \text{N}^+ + \text{O} \rightarrow \text{N} + \text{O}^+ \quad \text{no threshold} \]
  \[ \text{O}^+ + \text{N} \rightarrow \text{O} + \text{N}^+ \quad 0.92 \text{ V threshold} \]

- Example of oxygen atoms and molecules
  \[ \text{O}^+ + \text{O}_2 \rightarrow \text{O} + \text{O}_2^+ \quad \text{no threshold} \]
  \[ \text{O}_2^+ + \text{O} \rightarrow \text{O}_2 + \text{O}^+ \quad 1.4 \text{ V threshold} \]

- Charge transfer makes ions of easier-to-ionize neutrals
NEGATIVE ION LOSS

- Positive-negative ion recombination (mutual neutralization)
  \[ A^- + B^+ \rightarrow A + B^* \]

  ➞ large cross section; dominates negative ion destruction

- Electron detachment
  \[ e + A^- \rightarrow A + 2e \]

  Like “ionization” of \( A^- \); can be important
REACTION RATES

• Consider reaction
  \[ A + B \rightarrow \text{products} \]
  \[ \frac{dn_A}{dt} = -K_{AB} n_A n_B \]

• The rate coefficient is [p. 38]
  \[ K_{AB}(T) = \langle \sigma_{AB} v_R \rangle_{\text{Maxwellian}} \]
  \[ = \int_0^\infty f_m v_R \sigma_{AB}(v_R) 4\pi v_R^2 \, dv_R \]

• It often found to have an Arrhenius form
  \[ K_{AB} = K_{AB0} e^{-\mathcal{E}_a/T} \]
  \( \mathcal{E}_a \) = threshold or “activation” energy for the process
  \( K_{AB0} \) = “pre-exponential” factor (weakly depends on T)
• Consider the reactions

\[ A + B \xrightleftharpoons[K']{K} C + D \]

\( K \) has threshold or “activation” energy \( E_a \)

• From quantum mechanics and time reversibility

\[
m_R^2 g_A g_B v_R^2 \sigma(v_R) = m'_R^2 g_C g_D v'_R^2 \sigma'(v'_R)
\]

where

\[
m_R = \frac{m_A m_B}{m_A + m_B}, \quad m'_R = \frac{m_C m_D}{m_C + m_D}
\]

\[
\frac{1}{2} m_R v_R^2 = \frac{1}{2} m'_R v'_R^2 + e E_a
\]

The \( g \)'s are the degeneracies of the energy levels of the particles

• The boxed equation gives the relation between the cross sections for the forward and backward processes
Detailed Balancing (Cont’d)

- Integrate cross section relation [p. 167] over a Maxwellian distribution

\[
\frac{K(T)}{K'(T)} = \left(\frac{m'_R}{m_R}\right)^{3/2} \frac{\bar{g}_C \bar{g}_D}{\bar{g}_A \bar{g}_B} e^{-\mathcal{E}_a/T}
\]

- The \(\bar{g}\)'s are statistical weights (mean number of occupied states)
  \(\bar{g}_e = 2; \; \bar{g}_{\text{atom}} \sim 1–10; \; \bar{g}_{\text{mol}} \sim 100–1000\)
  \(\Rightarrow \bar{g}\)'s are given by thermodynamics

- The boxed equation gives the relation between the rate coefficients of the forward and backward processes

- Example

\[
e + A \xleftrightarrow[K_{\text{ex}}]{K_{\text{deexc}}} e + A^*
\]

\(K_{\text{ex}}\) (threshold energy \(\mathcal{E}_{\text{ex}}\)) is easy to measure or calculate
\(K_{\text{deexc}}\) is hard to measure or calculate, so use “detailed balancing”