Table 13.2 Hydrogenic atoms

The wavefunctions of hydrogenic atoms depend on three quantum numbers:

Principal quantum number: $n = 1, 2, 3, \ldots$

Angular momentum quantum number: $l = 0, 1, 2, \ldots, n-1$

Magnetic quantum number: $m_l = l, l-1, l-2, \ldots, -l$

The energy is related to n by

$$E_n = -\frac{hc\mathcal{R}}{n^2} \qquad hc\mathcal{R} = \frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

The magnitude of the orbital angular momentum of the electron $\{l(l+1)\}^{1/2}\hbar$ and its component on an arbitrary axis is $m_l\hbar$. Each energy level is n^2-fold degenerate.

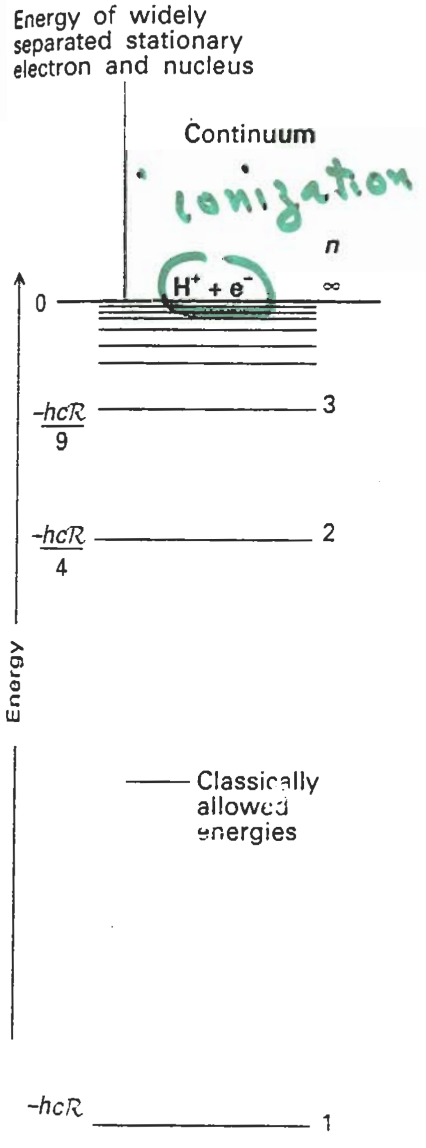
The wavefunctions are products of radial and angular components:

$$\psi = R(r)Y(\theta, \phi)$$

The angular wavefunctions Y are the spherical harmonics (Table 12.3) and the radial wavefunctions R are the normalized associated Laguerre polynomials multiplied by an exponential factor (Table 13.1).

The selection rules for spectroscopic transitions are

$$\Delta m_l = 0, \pm 1 \quad \Delta n \text{ unrestricted} \quad \Delta l = \pm 1$$



13.6 The energy levels of a hydrogen atom. The values are relative to an infinitely separated, stationary electron and a proton.

(a) The energy levels

The energy levels predicted by eqn 13 are depicted in Fig. 13.6. The energies, and also the separation of neighbouring levels, are proportional to Z^2, so the levels are four times as widely apart (and the ground state four times deeper in energy) in He^{+} ($Z = 2$) than in H ($Z = 1$). All the energies given by eqn 13 are negative. They refer to the bound states of the atom, in which the energy of the atom is lower than that of the infinitely separated, stationary electron and nucleus (which corresponds to the zero of energy). There are also solutions of the Schrödinger equation with positive energies. These solutions correspond to unbound states of the electron, the states to which an electron is raised when it is ejected from the atom by a high-energy collision or photon. The energies of the unbound electron are not quantized and form the continuum states of the atom.

Equation 13 is consistent with the spectroscopic result summarized by eqn 1, and we can identify the Rydberg constant for hydrogen ($Z = 1$) by writing

$$hc\mathcal{R}_H = \frac{\mu_H e^4}{32\pi^2\varepsilon_0^2\hbar^2} \qquad [17]$$

where μ_H is the reduced mass for hydrogen. The **Rydberg constant** itself, $\mathcal{R}$, is defined by the same expression except for the replacement of μ by the mass of an electron, m_e:

$$\mathcal{R}_H = \frac{\mu_H}{m_e}\mathcal{R} \qquad \mathcal{R} = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} \qquad [18]$$

Insertion of the values of the fundamental constants into the expression for $\mathcal{R}_H$ gives almost exact agreement with the experimental value. The only discrepancies arise from the neglect of relativistic corrections, which the non-relativistic Schrödinger equation ignores.

(b) Ionization energies

The ionization energy, I, of an element is the minimum energy required to remove an electron from the ground state, the state of lowest energy, of one of its atoms. The ground state of hydrogen is the state with $n = 1$, which has energy

$$E_1 = -hc\mathcal{R}_H$$