c. The accidental degeneracy of the hydrogen atom

Perhaps the most amazing feature of the expression for the hydrogenic energy is that it depends only upon the principal quantum number \( n \), and not upon the angular momentum quantum number \( \ell \). As remarked earlier, degeneracies are always associated with symmetries. We have already discussed the spatial symmetry associated with a central potential and the consequent degeneracy in \( m \), but to what symmetry does this "accidental degeneracy" correspond? The answer is that this symmetry is not apparent to ordinary humans, but, as will be discussed later, is associated with an additional constant of the classical motion that exists for the attractive \( 1/r \) potential that does not exist for other central potentials with the exception of the attractive \( r^2 \) potential, the three dimensional isotropic harmonic oscillator.

For a central potential we expect a \((2\ell + 1)\)-fold degeneracy because, as noted previously, there are \((2\ell+1)\) values of \( m \). That is, for any central potential there should be \((2\ell+1)\) energies corresponding to given values of \( n \) and \( \ell \) because the energy does not depend on \( m \). What then is the degree of the degeneracy for the hydrogen atom? To answer this question, we may sum over all of the \( m \)-values

\[
\text{degree of degeneracy} = \sum_{\ell = 1}^{n-1} (2\ell + 1) = 2 \sum_{\ell = 1}^{n-1} \ell + (n-1)\left(\frac{n}{2}\right) + n = n^2
\]

where the term \((n - 1)(n/2)\) arises from adding \((n - 1)\), \((n/2)\) times, a trick that has been attributed to Gauss as a schoolboy.

Spin adds a factor of 2, i.e. the degeneracy is \(2n^2\), but two proton spin states with respect to the spin of the electron add another two. Therefore, the total degeneracy of the hydrogen atom is \(4n^2\).

Although the effective potential, \( V_{\text{eff}}(r) \), is different for different values of \( \ell \) the energy of the hydrogen atom remains independent of \( \ell \). It depends only on the principal quantum number, \( n \), as shown in the figure. Since atomic units are in general use we have plotted the energy in "atomic units of energy", i.e. au. In this system the unit of charge is \( e \), the unit of mass is \( m \) (the mass of the electron) and the unit of angular momentum is \( \hbar \), i.e. \( e = m = \hbar = 1 \). These units lead to the first Bohr radius, \( a_0 \), as the unit of distance and the ionization energy of hydrogen being
1/2 au.

The figure illustrates the accidental degeneracy of the hydrogen atom by showing explicitly that the energies depend only on \( n \) and not \( \ell \). Notice that this diagram makes clear that the restriction on \( \ell \), i.e. \( 0 \leq \ell \leq (n - 1) \), which is obvious because the level is lower than the effective potential well, e.g. there can be no \( \ell = 2 \) level having \( n = 2 \) because the \( n = 2 \) energy is below \( V_{\text{eff}}(\rho) \) for \( \ell = 2 \).

\[
\begin{align*}
\ell = 1 & \quad \ell = 2 & \quad \ell = 3 \\
2 & \quad 4 & \quad 6 & \quad 8 & \quad 10 & \quad 12 & \quad 14 \\
n = 4 & \quad n = 3 & \quad n = 2 \\
-0.25 & \quad -0.2 & \quad -0.15 & \quad -0.1 & \quad -0.05 & \quad 0 & \quad 0.05 \\
\ell = 1 & \quad \ell = 0 \\
n = 1 \text{ at } -1.0 \text{ Ry} & \quad V_{\text{eff}}(\rho) = \frac{\ell (\ell + 1)}{\rho^2} - \frac{2}{\rho}
\end{align*}
\]

The energy levels of hydrogen superimposed on the effective potential curves, \( V_{\text{eff}}(\rho) \). The key point here is that the energies are independent of \( \ell \) and are thus the same regardless of the effective potential, provided that the value of \( \ell \) to which it corresponds is an allowed value.