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Quantitative calculation of the absorption spectrum of the hydrogen atom

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Abstract

With mathematical software (*Maple*), we have calculated quantitatively the entire absorption spectrum of the hydrogen atom in its electronic ground state for transitions to both discrete and continuum states, within the purview of non-relativistic wave mechanics. We present plots of wave functions in both coordinate and momentum representations and the calculated spectra.

Keywords: hydrogen atom, absorption spectrum, wave mechanics, coordinate and momentum representations

(Some figures may appear in colour only in the online journal)

1. Introduction

The solution of the hydrogen atom, as an embodiment of an electrostatic potential energy, according to non-relativistic wave mechanics is a common component of undergraduate courses in chemistry and physics, typically to produce the energies of the discrete states and the wave functions that are artefacts of this method of calculation. Schrödinger solved [1] this problem in a coordinate representation as the first result from his wave-mechanical treatment, although Pauli had previously derived [2] the energies of the discrete states with a symbolic approach related to matrix mechanics. An advance of the wave-mechanical method was the possibility of calculating *matrix elements* of a coordinate to various powers; the intensity of a spectral transition in absorption or emission according to an interaction between a molecule and the electric component of an electromagnetic wave is proportional to the square of such a matrix element of a coordinate to the first power. Although the typical solution of the hydrogen atom in various textbooks provides an application, to a real chemical entity, of

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the rules of quantum mechanics in general and of wave mechanics in particular, the mere production of those energies thereby is not novel, and the depictions of the wave functions are misleading if supposed to pertain to any system other than that comprising only one atomic nucleus and one electron.

In contrast with the circular orbits of Bohr and the elliptical orbits of Wilson and Sommerfeld that are absolutely unobservable, Heisenberg [3] understood that a proper physical treatment of a microscopic system must be concerned with the observable properties of such a system, specifically the frequencies and intensities of spectral lines connecting states of whatever entity comprises the system. A natural application of a calculation according to quantum mechanics within any algorithm is hence to calculate quantitatively an absorption spectrum, which is our objective in this work on the H atom; the spectrum includes not only the discrete spectral lines that connect discrete states, but also the absorption continuum for transitions of which the energy of the continuous states exceeds that of the threshold of ionization, $\mathrm{H} + h\nu \rightarrow \mathrm{H}^+ + e^-$. If this calculation is done manually, it is long and tedious; when we apply general mathematical software, in this case *Maple*, the calculation proceeds directly and the output is expressed in a mathematically meaningful manner. Here, we show the output from our calculations, not every step, but sufficient to illustrate the flow of the calculation and the explicit nature of the results.

2. Calculation of the discrete spectrum

After testing that no solution of the temporally independent Schrödinger equation for an atom of atomic number Z having one electron subject to an electrostatic attraction is practicable with Cartesian coordinates, we situate the atomic nucleus at the origin of a system of spherical polar coordinates, $r\,\theta\,\phi$; the resulting equation includes explicitly Planck constant h, electronic charge e, electronic mass μ and permittivity ε_0 of free space, with energy W:

$$
\begin{aligned}
Schreq := &-\frac{1}{4}\frac{h^2\left(\frac{\partial}{\partial r}\psi(r,\theta,\phi)\right)}{\pi^2\mu\, r} - \frac{1}{8}\frac{h^2\left(\frac{\partial^2}{\partial r^2}\psi(r,\theta,\phi)\right)}{\pi^2\mu} - \frac{1}{8}\frac{h^2\cos(\theta)\left(\frac{\partial}{\partial\theta}\psi(r,\theta,\phi)\right)}{\pi^2\mu\, r^2\sin(\theta)}\\
&-\frac{1}{8}\frac{h^2\left(\frac{\partial^2}{\partial\theta^2}\psi(r,\theta,\phi)\right)}{\pi^2\mu\, r^2} - \frac{1}{8}\frac{h^2\left(\frac{\partial^2}{\partial\phi^2}\psi(r,\theta,\phi)\right)}{\pi^2\mu\, r^2\sin(\theta)^2} - \frac{1}{4}\frac{Z\, e^2\psi(r,\theta,\phi)}{\pi\,\varepsilon_0\, r}\\
&= W\psi(r,\theta,\phi).
\end{aligned}
$$

The zero of the energy scale is defined by that electrostatic term according to which the atomic nucleus and electron are infinitely separate but stationary. The solution of this partial differential equation is directly expressed as a product of three separate functions of the coordinates,

$$
\begin{aligned}
solSeq := &\left(\psi(r,\theta,\phi) = \_F1(r)\_F2(\theta)\_F3(\phi)\right)\ \&\mathrm{where}\ \left[\left\{\frac{d^2}{dr^2}\_F1(r)\right.\right.\\
&= \frac{\_F1(r)\_c_1}{r^2\, h^2\,\varepsilon_0} - \frac{2\left(h^2\left(\frac{d}{dr}\_F1(r)\right)\varepsilon_0 + Z\, e^2\_F1(r)\pi\,\mu + 4\, W\_F1(r)\,\pi^2\,\mu\, r\,\varepsilon_0\right)}{h^2\, r\,\varepsilon_0},\\
&\frac{d^2}{d\theta^2}\_F2(\theta) = -\frac{\_F2(\theta)\_c_1}{h^2\,\varepsilon_0} + \frac{\_F2(\theta)\_c_2}{\sin(\theta)^2\, h^2\,\varepsilon_0} - \frac{\cos(\theta)\left(\frac{d}{d\theta}\_F2(\theta)\right)}{\sin(\theta)},\\
&\left.\left.\frac{d^2}{d\phi^2}\_F3(\phi) = -\frac{\_F3(\phi)\_c_2}{h^2\,\varepsilon_0}\right\}\right]
\end{aligned}
$$

of which each function is the solution of an ordinary differential equation of second order. After renaming the three functions, we proceed by solving first the Φ equation that contains only one parameter, $\_c_2$, from the separation; this solution is converted from sine and cosine functions to an exponential function,

$$Phisol := \Phi(\phi) = c1\ \mathrm{e}^{(m\,\phi\,I)}$$

in which, according to *Maple* notation, $I = \sqrt{-1}$, and integer m for a periodic condition takes as values positive and negative integers and zero. The parameter m is known as the magnetic quantum number. The integration constant $c1$ from the solution of the differential equation is evaluated as a normalization factor such that the integral of $\Phi(\phi)^*\ \Phi(\phi)$ for ϕ from 0 to $2\ \pi$ is equated to unity:

$$\int_0^{2\,\pi} \overline{(\Phi(\phi))}\ \Phi(\phi)\ \mathrm{d}\phi = 1.$$

The resulting normalized solution is

$$Phisol := \Phi(\phi) = \frac{1}{2}\frac{\sqrt{2}\ \mathrm{e}^{(m\,\phi\,I)}}{\sqrt{\pi}}.$$

As a result of this solution, the Θ equation also contains, as a parameter, m, instead of $\_c_2$:

$$Thetaeq := \frac{\mathrm{d}^2}{\mathrm{d}\theta^2}\Theta(\theta) = \frac{-\Theta(\theta)\_c_1 + \Theta(\theta)\_c_1\cos(\theta)^2 + \Theta(\theta)\ m^2h^2\varepsilon_0 - \cos(\theta)\ \left(\frac{\mathrm{d}}{\mathrm{d}\theta}\Theta(\theta)\right)\ h^2\varepsilon_0\sin(\theta)}{h^2\varepsilon_0\sin(\theta)^2}.$$

To solve this ordinary differential equation in a convenient form, we undertake a change of variable, from θ to $\arccos(x)$, solve the equation and reverse the change of variable to produce this result that contains two independent solutions,

$$Thetasol := \Theta(\cos(\theta)) = \_C1\ \mathrm{LegendreP}\left(\frac{1}{2}\frac{\sqrt{4\_c_1 + h^2\varepsilon_0} - h\sqrt{\varepsilon_0}}{h\sqrt{\varepsilon_0}},\ m,\ \cos(\theta)\right) + \_C2\ \mathrm{LegendreQ}\left(\frac{1}{2}\frac{\sqrt{4\_c_1 + h^2\varepsilon_0} - h\sqrt{\varepsilon_0}}{h\sqrt{\varepsilon_0}},\ m,\ \cos(\theta)\right)$$

in which Legendre functions appear in two forms. We eliminate the LegendreQ function because it has a logarithmic singularity. To make $\Theta(\cos(\theta))$ periodic in θ, the first parameter as argument of the remaining LegendreP function must be an integer, which we denote as l and call the azimuthal quantum number, yielding this form,

$$Thetasol := \Theta(\cos(\theta)) = c2\ \mathrm{LegendreP}(l,\ |m|,\ \cos(\theta))$$

for a physically acceptable solution, only the magnitude of m is a meaningful argument in this context. As direct normalization of this function $\Theta(\theta)$ is impracticable in one step because it involves two parameters, l and $|m|$, we invoke from the literature this formula to replace $c2$,

$$c2 := \frac{1}{2}\sqrt{2}\sqrt{\frac{(1 + 2\ l)\ (l - |m|)!}{(l + |m|)!}}$$

so as to produce the complete solution of the Θ equation:

$$Thetasol := \Theta(\cos(\theta)) = \frac{1}{2}\sqrt{2}\sqrt{\frac{(1 + 2\ l)\ (l - |m|)!}{(l + |m|)!}}\ \mathrm{LegendreP}(l,\ |m|,\ \cos(\theta)).$$

Like the unit of Φ, the unit of Θ is the inverse square root of the dimensionless unit of angle, explicitly rad$^{-1/2}$. A product of $\Theta(\theta)$ and $\Phi(\phi)$ is called a spherical harmonic, generally denoted as $Y(\theta, \phi)$. As the physical unit of $Y(\theta, \phi)$ is the inverse square root of solid angle—sr$^{-1/2}$, which is dimensionless, the unit of $Y(\theta, \phi)$ becomes rad^{-1}.

In implementing the solution of the radial equation for $R(r)$, we expand it,

$$Req2 := \frac{\mathrm{d}^2}{\mathrm{d}r^2}R(r) = \frac{R(r)\,l}{r^2} + \frac{R(r)\,l^2}{r^2} - \frac{2\left(\frac{\mathrm{d}}{\mathrm{d}r}R(r)\right)}{r} - \frac{2\,Z\,e^2\,R(r)\,\pi\,\mu}{h^2\,r\,\varepsilon_0} - \frac{8\,W\,R(r)\,\pi^2\,\mu}{h^2}$$

observe that it contains l as a parameter and proceed to solve it:

$$Rsol := R(r) = \frac{\_C1\ \mathrm{WhittakerM}\left(-\frac{1}{4}\frac{Z\,e^2\sqrt{\mu}\sqrt{2}}{h\,\varepsilon_0\sqrt{-W}}\right),\ l+\frac{1}{2},\ -\frac{4\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}\,r}{h}}{r} + \frac{\_C2\ \mathrm{WhittakerW}\left(-\frac{1}{4}\frac{Z\,e^2\sqrt{\mu}\sqrt{2}}{h\,\varepsilon_0\sqrt{-W}},\ l+\frac{1}{2}, -\frac{4\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}\,r}{h}\right)}{r}.$$

As expected, this result contains two independent solutions, of which the WhittakerW function shows unphysical behaviour and must be eliminated. To ensure the correct signs of the arguments of the WhittakerM function, we replace $2^{1/2}$ by $-2^{1/2}$:

$$Rsol := \frac{\_C1\ \mathrm{WhittakerM}\left(\frac{1}{4}\frac{Z\,e^2\sqrt{\mu}\sqrt{2}}{h\,\varepsilon_0\sqrt{-W}},\ l+\frac{1}{2},\ \frac{4\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}\,r}{h}\right)}{r}.$$

Although a solution of this radial equation in terms of WhittakerM functions is perfectly acceptable and viable, to conform to tradition we convert these functions into a product of an exponential function and a generalized LaguerreL function in two steps, through intermediate KummerM functions so as to ensure the appropriate arguments of the eventual LaguerreL functions:

$$Rsol := \_C1\,\mathrm{e}^{\left(-\frac{2\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}\,r}{h}\right)}\left(\frac{4\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}r}{h}\right)^{(1+l)} \mathrm{Kummer\,M}\left(1+l-\frac{1}{4}\frac{Ze^2\sqrt{\mu}\sqrt{2}}{h\varepsilon_0\sqrt{-W}},\ 2+2l,\ \frac{4\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}r}{h}\right)\Bigg/ r\,.$$

The arguments of KummerM functions therein are purely real because, for the bound states of the H atom of interest in this part of the total calculation, energies W are negative. The next transformation generates the desired Laguerre functions:

$$Rsol := \_C1\,\mathrm{e}^{\left(-\frac{2\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}\,r}{h}\right)}\left(\frac{4\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}r}{h}\right)^{(1+l)} \mathrm{LaguerreL}\left(-1-l+\frac{1}{4}\frac{Ze^2\sqrt{\mu}\sqrt{2}}{h\varepsilon_0\sqrt{-W}},\ 1+2l,\ \frac{4\pi\sqrt{2}\sqrt{-W}\sqrt{\mu}r}{h}\right)\Bigg/ \left(r\ \mathrm{binomial}\left(1+l+\frac{1}{4}\frac{Ze^2\sqrt{\mu}\sqrt{2}}{h\varepsilon_0\sqrt{-W}},\ -1-l+\frac{1}{4}\frac{Ze^2\sqrt{\mu}\sqrt{2}}{h\varepsilon_0\sqrt{-W}}\right)\right).$$

So that the solution $R(r)$ has acceptable behaviour as $r \to \infty$, the first argument of those Laguerre functions must be a non-negative integer, named k, and known as the radial quantum number:

$$Lag2 := -1 - l + \frac{1}{4}\frac{Ze^2\sqrt{\mu}\sqrt{2}}{h\varepsilon_0\sqrt{-W}} = k.$$

Solving for the energy W_k of the bound states then yields

$$Wk := -\frac{1}{8}\frac{Z^2e^4\mu}{h^2\varepsilon_0^2(1+l+k)^2}.$$

As both k and l are non-negative integers, their sum with unity must be a positive integer, denoted as n and called the energy quantum number, producing energies W_n of bound states in this ultimate formula:

$$Wn := -\frac{1}{8}\frac{Z^2e^4\mu}{h^2\varepsilon_0^2n^2}.$$

To express the radial function $R(r)$ in its ultimate form, we again invoke from the literature a normalization factor because its direct evaluation involving two parameters, n and l, is impracticable in one step:

$$\begin{aligned} Rsol := R(r) = 2h^{(-2-2l)}e^{(2+2l)}\sqrt{\frac{\pi\mu e^2 Z(1+l+n)!(1+l+n)}{\varepsilon_0 h^2(n-l-1)!}}(n-l-1)! \\ \mathrm{LaguerreL}\left(n-l-1,\ 1+2l,\ \frac{2\pi Ze^2\mu r}{h^2\varepsilon_0 n}\right)\pi Z\mu\left(\frac{2\mu\pi rZ}{\varepsilon_0 n}\right)^l \mathrm{e}^{\left(-\frac{\pi Ze^2\mu r}{h^2\varepsilon_0 n}\right)} \Big/ \\ (n^2(1+l+n)!\varepsilon_0). \end{aligned}$$

The SI unit of $R(r)$ is $\mathrm{m}^{-3/2}$. The total amplitude function $\psi(r, \theta, \phi)$ is hence a product of the three solutions of the separate ordinary differential equations:

$$\begin{aligned} \psi := h^{(-2-2l)}e^{(2+2l)}\sqrt{\frac{\pi\mu e^2 Z(1+l+n)!(1+l+n)}{\varepsilon_0 h^2(n-l-1)!}}(n-l-1)! \\ \mathrm{LaguerreL}\left(n-l-1,\ 1+2l,\ \frac{2\pi Ze^2\mu r}{h^2\varepsilon_0 n}\right)\sqrt{\pi}\, Z\mu\left(\frac{2\mu\pi rZ}{\varepsilon_0 n}\right)^l \mathrm{e}^{\left(-\frac{\pi Ze^2\mu r}{h^2\varepsilon_0 n}\right)} \\ \sqrt{\frac{(1+2l)\ (l-|m|)!}{(l+|m|)!}}\ \mathrm{LegendreP}(l, |m|, \cos(\theta))\, e^{(m\phi I)}/(n^2(1+l+n)!\varepsilon_0) \end{aligned}$$

to which the time factor might be added from the temporally dependent Schrödinger equation, but that is immaterial for the purposes here.

This point in a typical treatment of the H atom, for which $Z = 1$, according to non-relativistic wave mechanics is generally the terminus apart from plots of the various functions in two or three dimensions. We refrain from presenting such plots except radial functions $\Psi(r, \theta, \phi)$ for $1 \leqslant n \leqslant 5$ and $l = m = 0$ in figure 1, for comparison with a subsequent plot. For the H atom in the electronic ground state, denoted as $1\ ^2\mathrm{S}_{1/2}$, the red curve of $4\ \pi\ r^2\ \psi(1, 0, 0)^2$ in figure 1 exhibits a single maximum, whereas for electronically excited states, denoted as $n\ ^2\mathrm{S}_{1/2}$, the other curves of $4\ \pi\ r^2\ \psi(n, 0, 0)^2$ exhibit n maxima that extend to increasing distance between the electron and the atomic nucleus as n increases from 2 to 5.

As an application of the information that we have derived in the form of energies and wave functions of discrete states, we proceed to calculate the absorption spectrum of the H atom in

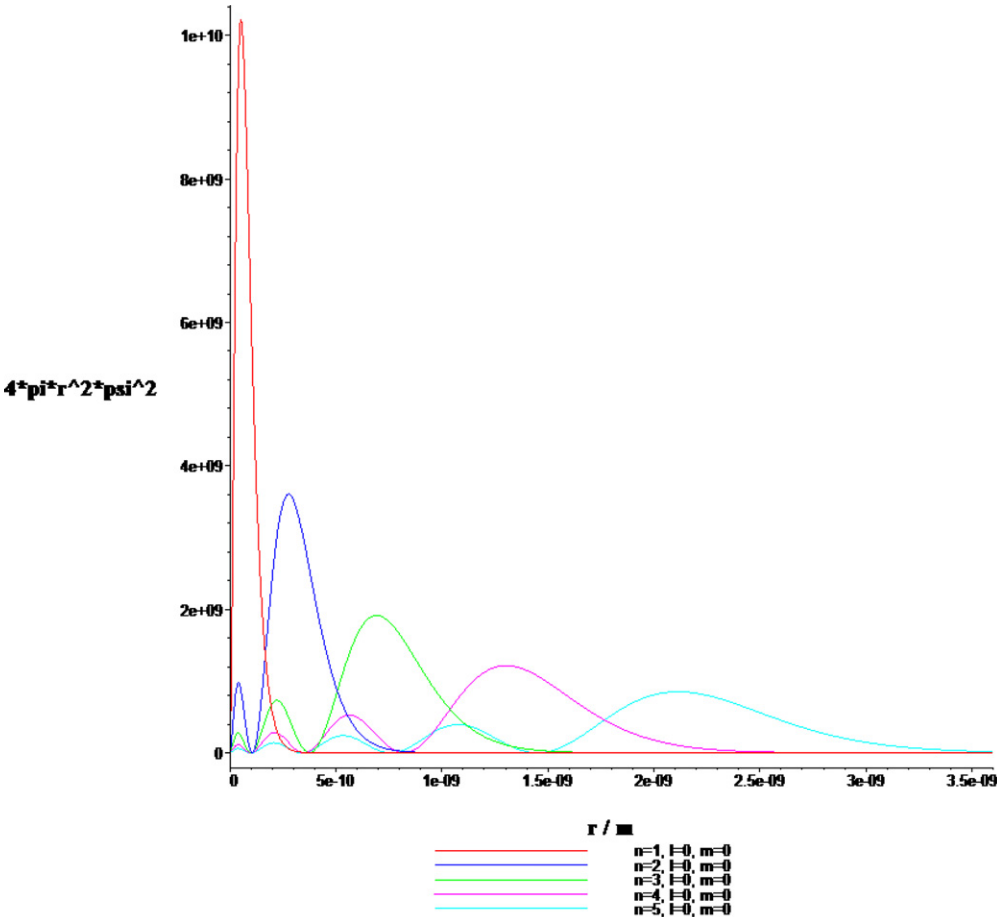

Figure 1. Curves of $4\pi\ r^2\ \psi(r, \theta, \phi)^2$ for states of H with quantum numbers $1 \leqslant n \leqslant 5$, $l = 0$, $m = 0$.

electric-dipolar transitions from its electronic ground state, 1 $^2S_{1/2}$, to electronically excited states, $n\ ^2P_{1/2,3/2}$, which are observable as lines in the Lyman series in the vacuum-ultraviolet region of the electromagnetic spectrum. According to Dirac's procedure [4], the intensity of a spectral line is proportional to the square of a matrix element for electric-dipolar moment involving the wave functions of the combining states in this triple integral:

$$\langle e\ z\rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi\,(n', l', m')^* e\,r^3 \cos(\theta)\ \psi\,(n, l, m) \sin(\theta)\ \mathrm{d}\phi\ \mathrm{d}\theta\ \mathrm{d}r.$$

For a transition from a state with which is associated wave function $\psi(n, l, m)$ to another state with wave function $\psi(n', l', m')$ according to the component z of electric dipolar moment, the triple integral over coordinates $r\ \theta\ \phi$ has, as factors in the integrand, the wave functions of the combining states, $e\ r\ \cos(\theta)$ as that component $e\ z$ and integrating factor $r^2\ \sin(\theta)$. For the transitions of interest, the state of origin is defined with quantum numbers $n = 1$, $l = 0$, $m = 0$ and accordingly wave function $\psi(1, 0, 0)$,

$$\psi\,(1,\ 0,\ 0) = \frac{e^3 \mu^{(3/2)} \pi\,\mathrm{e}^{\left(-\frac{\pi e^2 \mu r}{h^2 \varepsilon_0}\right)}}{h^3 \varepsilon_0^{(3/2)}}$$

and the terminal state is defined with quantum numbers $n > 1$, $l = 1$, $m = 0$ and accordingly wave function $\psi(n,\ 1,\ 0)$. The transition of least energy difference is to a state $n = 2$, $l = 1$, $m = 0$ with this wave function:

$$\psi(2,\ 1,\ 0) = \frac{1}{8}\,\frac{\sqrt{2}e^5\mu^{(5/2)}\pi^2 r\,\mathrm{e}^{\left(-1/2\,\frac{\pi e^2\mu r}{h^2\varepsilon_0}\right)}\cos(\theta)}{h^5\varepsilon_0^{(5/2)}}.$$

Inserting these quantities into the formula above for matrix element $\langle 2,\ 1,\ 0 \mid e\,z \mid 1,\ 0,\ 0\ \rangle$ yields this exact result:

$$\langle ez\rangle := \frac{128}{243}\,\frac{h^2\varepsilon_0\sqrt{2}}{e\pi\mu}.$$

The optical frequency of a transition is related to the energy difference,

$$\nu = \left|\frac{W_n}{h} - \frac{W_{n'}}{h}\right|$$

which for the same particular transition yields this exact result:

$$\nu_2 := \frac{3}{32}\,\frac{\mu e^4}{h^3\varepsilon_0^2}.$$

The most meaningful measure of the intensity of a transition is the dimensionless oscillator strength or f value, related to that frequency and the square of the electric-dipolar transition moment as

$$f = \frac{8}{3}\,\frac{\pi^2 m_e}{he^2}\,\nu\langle e\,z\rangle^2.$$

For the same particular transition above, evaluation of that formula yields this exact result:

$$f_2 := \frac{8192}{19\,683}.$$

We show in figure 2 the first ten lines in the Lyman series plotted as vertical lines, of which the stature is equal to $\log_{10}(10^3\ f)$, versus frequency ν/PHz of the transitions.

The sequence of lines clearly converges to a limit at a frequency as $k \to \infty$:

$$\nu = R\left(\frac{1}{1^2} - \frac{1}{k^2}\right)$$

in which the Rydberg constant R has frequency units. That limit has frequency

$$\nu_\infty = 0.328\ 805\ 1240\ 10^{16}\ \mathrm{Hz}$$

equivalent to wavenumber 10 967 758.37 m^{-1} and wave length 91.175 nm. The energy of photons at that limit defines a unit of energy called Rydberg, denoted by Ry, which has a value of approximately 13.598 eV.

The oscillator strengths of these lines in absorption evidently decrease rapidly with increasing quantum number n of the excited state; an exact formula to represent this variation is readily fitted to the exact results to yield this result for a transition from a state with $n = 1$, $l = 0$, $m = 0$ to a state with $n = k$, $l = 1$, $m = 0$:

$$f_k = \frac{256\,k^5(k-1)^{(2k-4)}}{3(k+1)^{(2k+4)}}.$$

The partial sum of these oscillator strengths for the first 500 transitions, calculated as an exact fraction, is converted to approximately 0.5650.

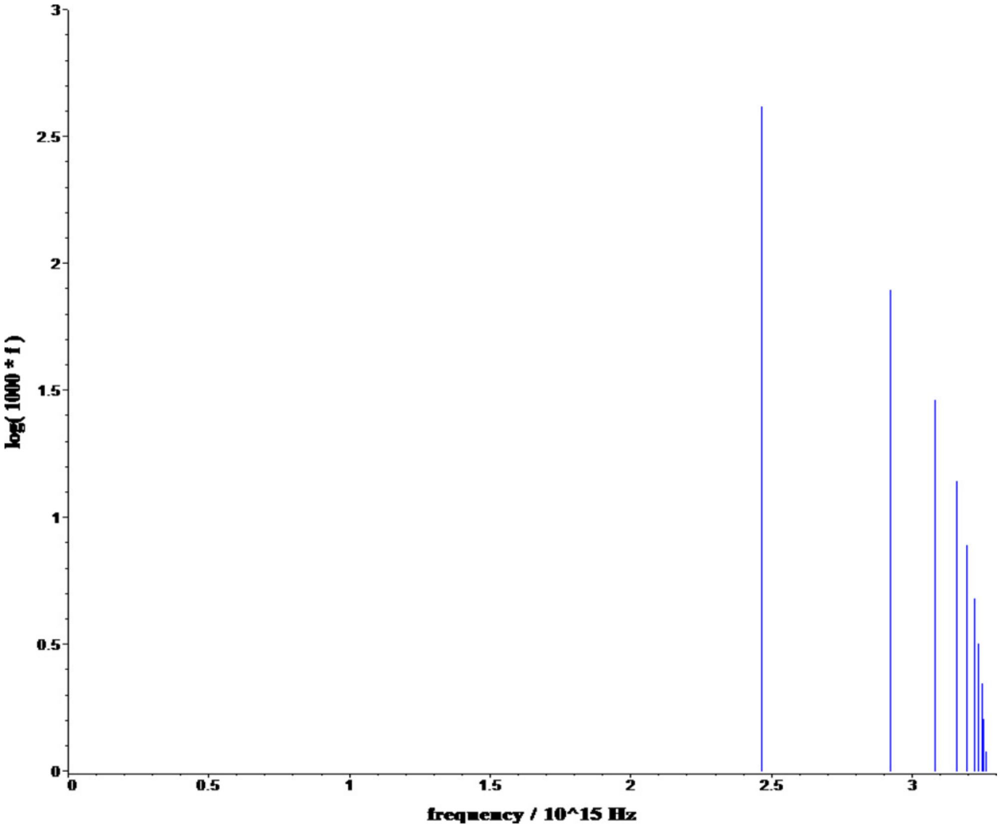

Figure 2. Absorption spectrum of H in the vacuum-ultraviolet region.

3. Calculation of the continuous spectrum

Illumination of hydrogen atoms with light of frequency greater than, or of wave length less than, the limiting value in the Lyman series results in ionization,

$$\mathrm{H} + h\nu - > \mathrm{H}^{+} + e^{-}, \ \ \nu > 3.29\ 10^{15}\,\mathrm{Hz}$$

for which, as the frequency of ionizing radiation exceeds that limit, the electron acquires correspondingly increased kinetic energy. To extend the calculation of the spectrum beyond the ionization limit shown above, we require a wave function for the H atom for energies greater than the ionization energy. As the corresponding calculations can no further be made exactly, we proceed to work numerically in atomic units, such that $m_e = e = 1$, $h = 2\,\pi$, and the unit of length is the Bohr constant a_0. The atomic unit of energy is the hartree, denoted as E_h, but we work here in terms of the Rydberg; 1 Ry $= E_h/2$.

For the integrals of transition moment $\langle e\,z\rangle$, we require a wave function for the ionized states, which we express in terms of a radial factor incorporating the KummerM functions, adapted from Bethe and Salpeter [5], that we show above as an intermediate between the WhittakerM and LaguerreL functions for the discrete states; because here energy $E > 0$, the arguments of the KummerM functions become complex and conversion to LaguerreL functions is no longer practicable:

$$\mathrm{Rc}(Z, E, l, r) = 2\sqrt{E}\ \mathrm{e}^{\left(\frac{\pi Z\sqrt{2}}{4\sqrt{E}}\right)} \left|\Gamma\left(l+1+\frac{\frac{1}{2}IZ\sqrt{2}}{\sqrt{E}}\right)\right| (2\sqrt{2}\sqrt{E}\ r)^{l}\ \mathrm{e}^{(-I\sqrt{2}\sqrt{E}\ r)}$$
$$\mathrm{KummerM}\left(l+1\frac{\frac{1}{2}IZ\sqrt{2}}{\sqrt{E}},\ 2+2l, 2I\sqrt{2}\sqrt{E}\ r\right) \Big/ ((1+2l)!\sqrt{\pi\sqrt{2}\sqrt{E}}).$$

Although the arguments of the KummerM functions are complex, the wave functions are real. For the states of continuous energy, the energy E itself serves, rather than a quantum number corresponding to n applicable to the discrete states. For the electronic ground state $1\ ^2\mathrm{S}_{1/2}$ that is the same origin of transitions as for the Lyman series, the wave function in atomic units becomes

$$\mathrm{psils} := \frac{\mathrm{e}^{(-r)}}{\sqrt{\pi}}$$

in the normalized form. We plot in figure 3 the radial wave functions from $r = 0$ to 50 a_0 for energies/Ry of magnitudes 10^{-7}, 0.1 and 10, with the wave function for the electronic ground state for comparison.

The curves for the continuous states show an oscillatory behaviour that persists as $r \to \infty$, as expected because a wave function for a free particle has a purely sinusoidal form; here, the increased amplitudes of the oscillation towards $r = 0$ result from the electrostatic attraction. Because these wave functions for the continuous states retain an oscillatory amplitude at large distances between the electron and the atomic nucleus, normalization over the entire domain of that distance is impracticable; for that reason, these continuum wave functions are normalized over energy [5], not distance, as follows:

$$\int_0^{\infty} \mathrm{Rc}(Z, E, l, r)\, r^2\, \mathrm{d}r \int_{E-\Delta E}^{E+\Delta E} \mathrm{Rc}(Z, E', l, r)\, \mathrm{d}E' = 1.$$

The above formula for the radial part of the wave functions for the continuous states incorporates that normalization. The angular parts of the total wave function, independent of time, for the continuous states are the same spherical harmonics, $\mathrm{Y}(\theta, \phi)$, as for the discrete states.

The triple integral to calculate the electric-dipolar moment in atomic units for the transition of the H atom from the electronic ground state $1\ ^2\mathrm{S}_{1/2}$ to a state of continuous energy E above the threshold for ionization becomes accordingly

$$\langle e\, z\rangle = \frac{1}{a_0}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \frac{1}{3}E\ \mathrm{e}^{\left(\frac{\pi\sqrt{2}}{4\sqrt{E}}\right)} \left|\Gamma\left(2+\frac{\frac{1}{2}I\sqrt{2}}{\sqrt{E}}\right)\right| \sqrt{2}\ r^4\ \mathrm{e}^{(-I\sqrt{2}\sqrt{E}\ r)}$$
$$\mathrm{KummerM}\left(2+\frac{\frac{1}{2}I\sqrt{2}}{\sqrt{E}},\ 4, 2I\sqrt{2}\sqrt{E}\ r\right) \sqrt{3}\ \cos(\theta)^2\ \mathrm{e}^{(-r)}\ \sin(\theta)/$$
$$\left(\sqrt{\pi\sqrt{2}\sqrt{E}\pi}\right)\ \mathrm{d}\phi\, \mathrm{d}\theta\, \mathrm{d}r.$$

The formula in atomic units for the oscillator strength for a transition into the continuum as a function of energy E/Ry is [5]

$$f(E) = \langle ez\rangle^2(1+E),$$

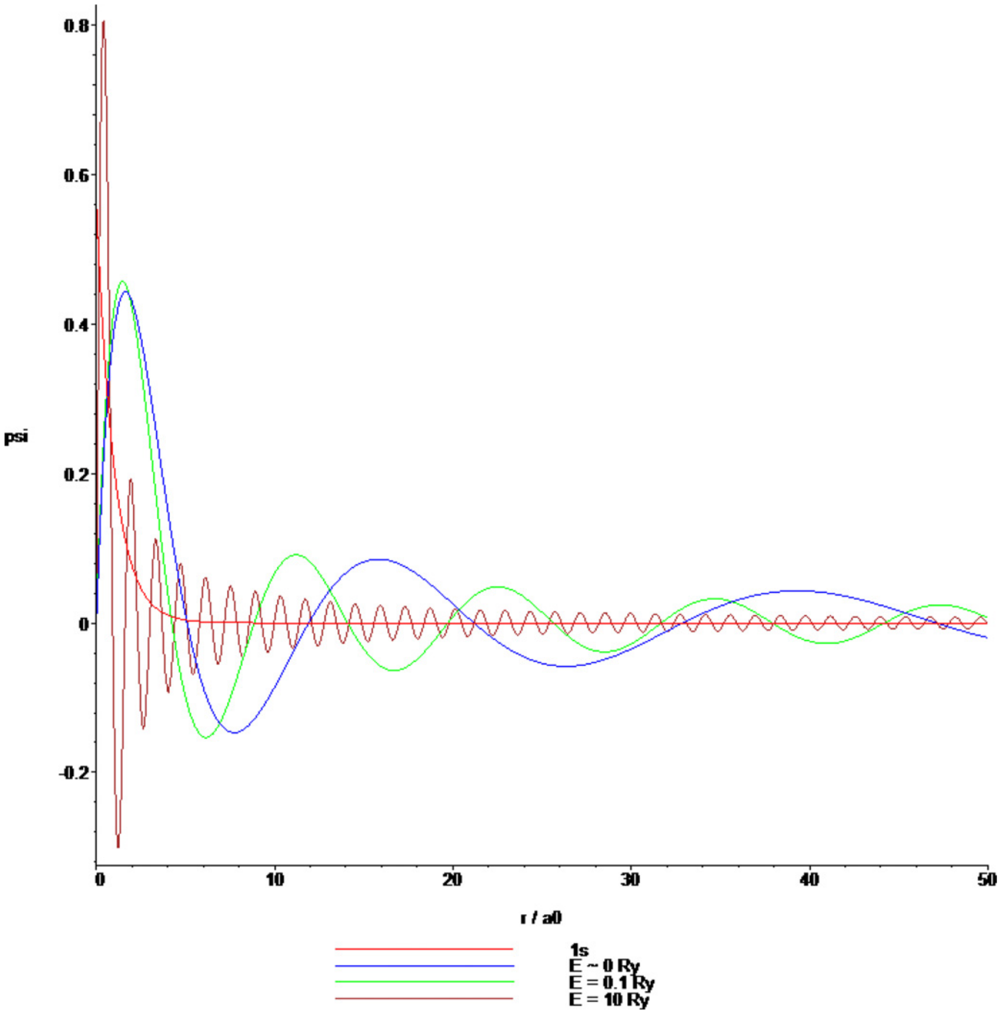

Figure 3. Curves of radial wave functions of H according to the coordinate representation in atomic units for discrete ground state 1 $^2S_{1/2}$ and for states in the continuum with energy/Ry 10^{-7}, 0.1 and 10.

yielding the plot in figure 4 of the resulting oscillator strength/per unit energy as a function of energy for the first Rydberg above the threshold of ionization, and the plot in figure 5 of oscillator strength on a logarithmic scale for the first 200 Ry above the threshold of ionization.

The oscillator strength per unit energy for the continuum clearly decreases rapidly from its value at the onset of ionization. A numerical integration of the area under the curve from 10^{-7} to 200 Ry yields a total oscillator strength for the continuum equal to 0.4350.

4. Discussion

The discrete spectrum of H shown in figure 1 for lines in the Lyman series and the continuous spectrum shown in figures 4 and 5 together constitute the total and entire absorption spectrum of the H atom in its electronic ground state, within the confines of the algorithm for the solution

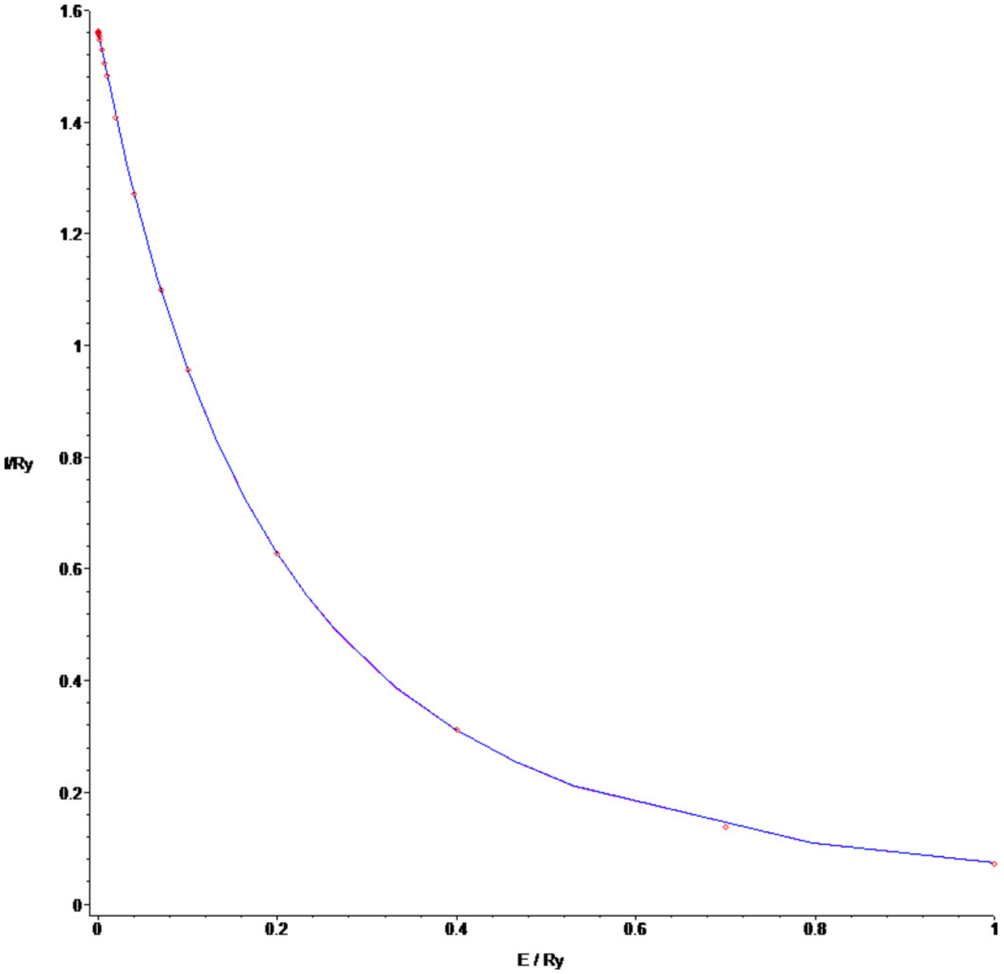

Figure 4. Oscillator strength f/Ry for transitions of H from discrete ground state $1\ ^2S_{1/2}$ to states in the continuum up to 1 Ry above the threshold for ionization.

according to the Schrödinger equation independent of time. Because that solution yields only three quantum numbers—n l m—corresponding to three spatial variables—x y z or r θ ϕ, there is no account of the intrinsic angular momenta of the electron and the atomic nucleus, a proton in the case of ^{1}H. An alternative strategy involves parabolic coordinates [5] for which an algebraic treatment is equally practicable. A relativistic treatment with Dirac's equation to generate $\psi(x, y, z, t)$ yields four quantum numbers—$n\ l\ m_l\ m_s$—and consequently not only fine structure of the optical spectral lines, which Shrum [6] measured first for the Balmer series in emission, but also a further line at radio frequencies. The intrinsic angular momenta of the proton and electron add vectorially to generate two substates within $1\ ^2S_{1/2}$ of which the frequency associated with the difference of energies is 1.42 GHz, hence in the radio-frequency region; the corresponding oscillator strength, for a magnetic-dipolar transition, is $f = 1.94\ 10^{-12}$, so negligible in relation to the optical transitions. The sum of the total oscillator strengths for the discrete and continuous spectra is unity, in accordance with the sum rule of Thomas, Reiche and Kuhn. Such that the total oscillator strength equals the number of electrons in the system. In our calculation, we have neglected the distinction between the origin of the

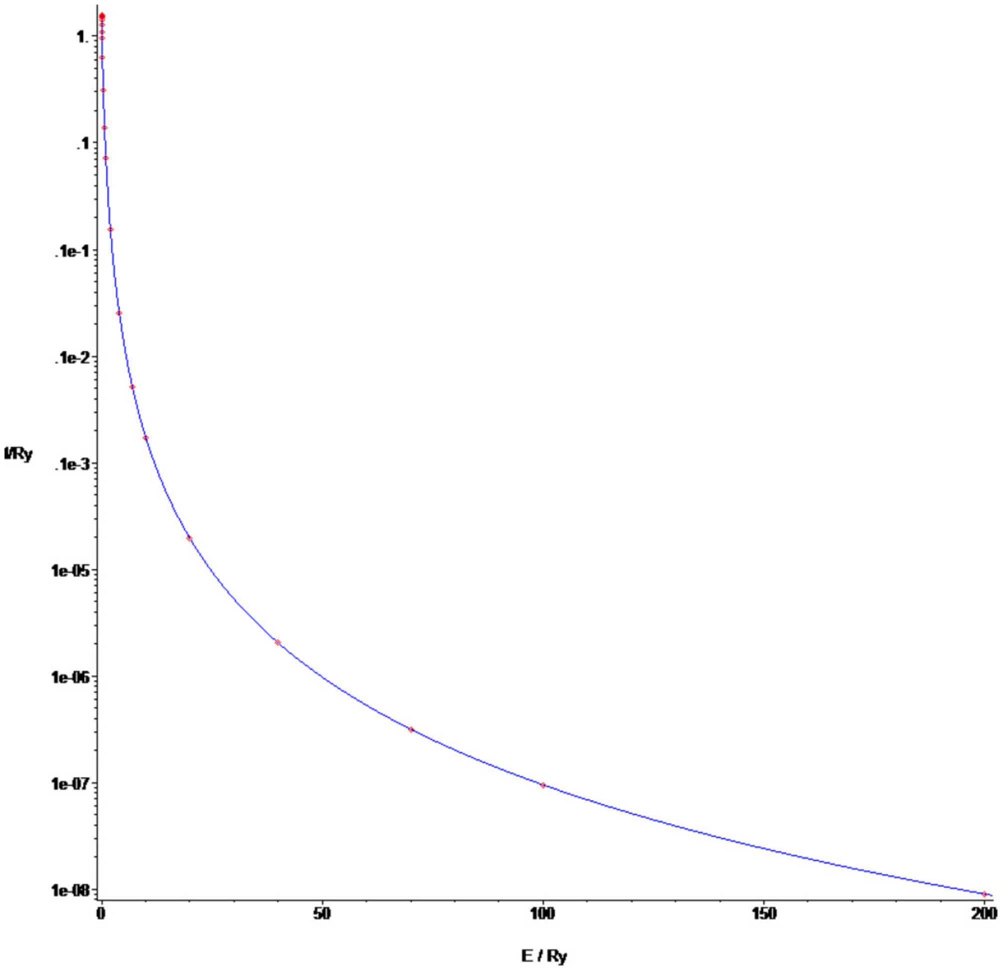

Figure 5. Oscillator strength f/Ry on a logarithmic scale for transitions of H from discrete ground state 1 $^2\mathrm{S}_{1/2}$ to states in the continuum up to 200 Ry above the threshold for ionization.

coordinates and the centre of mass of the atomic system and related aspects, which only slightly affect the overall results.

This derivation demonstrates the power of mathematical software not merely to generate wave functions and energies, exactly within the purview of Schrödinger's temporally independent equation, but especially to generate meaningful data for direct and quantitative comparison with experiment. The formulae and graphs were extracted into this report from a *Maple* worksheet that required for its execution only 12 s for the discrete spectrum and properties, and a further 300 s for the continuous spectrum, excepting some slow numerical integrations of the oscillator strength for the continuum states with energies greater than 4 Ry above the ionization threshold. Of that duration, 84 s were required to produce the plot of the continuum wave functions, in figure 3, and 130 s were devoted to a calculation, not shown, of a ratio of squares of a continuum wave function for $E = 1$ Ry for 50 a_0 and 100 a_0 that demonstrates the lack of convergence of that wave function. The total duration also included several other plots of wave functions and many calculations to prove the normalization and

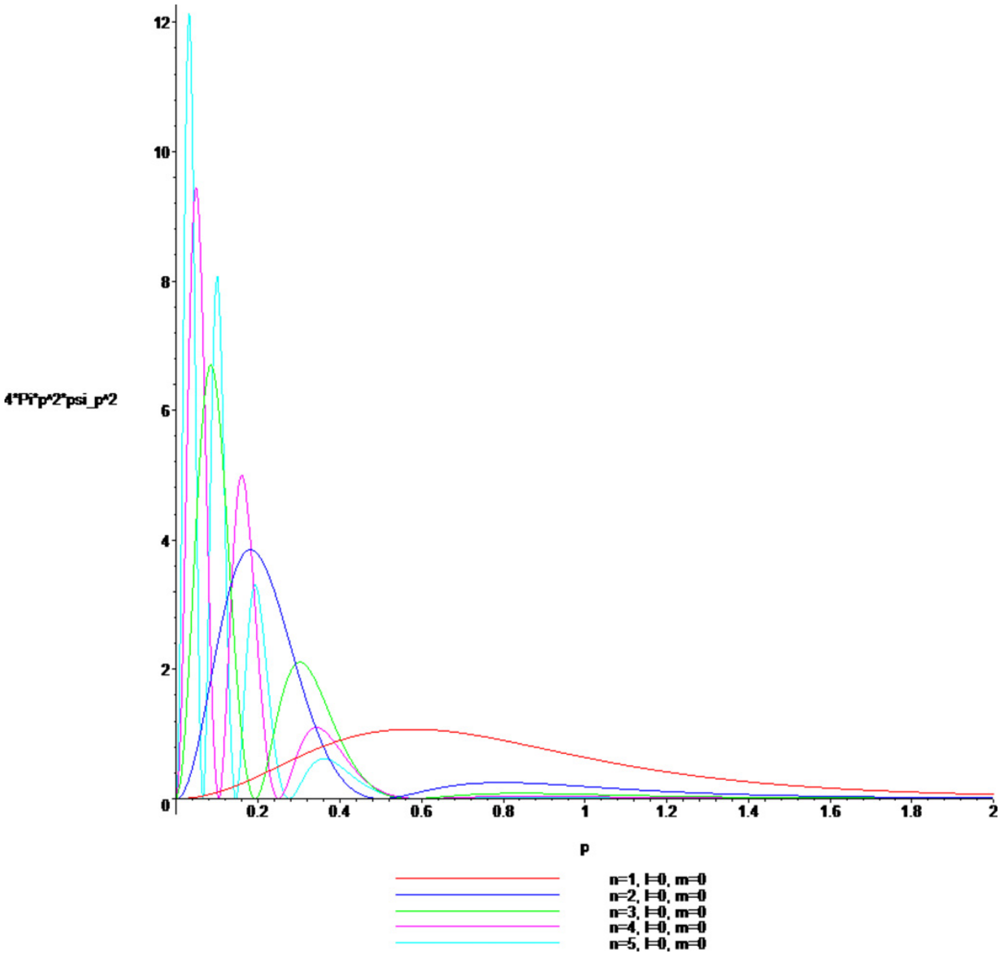

Figure 6. Curves of radial wave functions $4\pi p^2\ \psi(p)^2$ of H in atomic units according to the momentum representation for states with quantum numbers $1 \leqslant n \leqslant 5$, $l = 0$, $m = 0$.

orthogonality of the wave functions of the discrete and continuum states. The production of the commands for the entire worksheet required several hours, including trial and error—in a spirit of constructive and experimental mathematics—to find the best conditions to yield the desired results. The entire effort naturally requires a much shorter duration than any derivation performed only by hand, but the results of quantitative and accurate calculations and illuminating plots are far superior to what can be achieved by manual means.

Our calculation of observable properties of an H atom, namely the frequencies and intensities of its absorption spectrum, is made with Schrödinger's equation in a coordinate representation. The alternative momentum representation yields the same results for observable properties, but the derivation of those wave functions involves an integral equation, so more difficult than that involving a partial-differential equation. Accepting the reported result for the momentum wave functions in atomic units [5], we plot, in figure 6 in atomic units, the squares of the radial components of those momentum wave functions, $4\pi\ p^2\ \psi(p)^2$, for spherically symmetric states according to quantum numbers $1 \leqslant n \leqslant 5$, $l = 0$ and $m = 0$, for direct comparison with the corresponding plots of the squares of the coordinate wave functions, effectively $4\pi r^2\ \psi(r)^2$, in figure 1.

For the H atom in the electronic ground state, $1\ ^2\mathrm{S}_{1/2}$, the red curve in figure 6 exhibits a single maximum for $p > 0$; for electronically excited states, $n\ ^2\mathrm{S}_{1/2}$, the other curves exhibit n maxima but become compressed toward $p = 0$, instead of expanding to greater r for the coordinate wave functions in figure 1. This behaviour is consistent with the conjugate nature of the coordinate and momentum variables. All curves are symmetric about $p = 0$. The use of those momentum wave functions instead of coordinate wave functions yields the same oscillator strengths in principle and in practice according to our direct calculations.

Acknowledgment

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