Electrons above a helium surface and the one-dimensional Rydberg atom

Michael Martin Nieto*

Theoretical Division (MS-B285), Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545
(Received 13 September 1999; published 11 February 2000)

Isolated electrons resting above a helium surface are predicted to have a bound spectrum corresponding to a one-dimensional hydrogen atom. But in fact, the observed spectrum is closer to that of a quantum-defect atom. Such a model is discussed and solved in analytic closed form.

Some time ago the prediction was made that an isolated electron resting on a helium (or some certain other) surface should have a bound-state spectrum in the vertical direction [1–3]. The idea is that the electron induces an image charge in the helium, producing a potential on the electron of

$$V(x) = -\frac{Ze^2}{x}, \quad x>0, \quad Z = \frac{(\epsilon-1)}{4(\epsilon+1)}, \tag{1}$$

$$= +\infty, \quad x \leq 0, \tag{2}$$

where ϵ is the dielectric constant [4]. For helium it is [5,6]

$$\epsilon = 1.05723, \quad Z = 0.0069547. \tag{3}$$

The spectrum should thus be similar to that of a (weakly coupled) one-dimensional hydrogen atom. This phenomenon has been observed [6–8]. (See Ref. [9] for a current review and [10] for a proposed application to quantum computing.)

Consider the one-dimensional Schrödinger equation of this system [11]:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \frac{Ze^2}{x} \right)\psi_n(x) = E_n\psi_n(x). \tag{4}$$

Making the changes of variables

$$E_n = -\frac{\mathcal{E}_0}{n^2}, \quad \mathcal{E}_0 = \frac{mZ^2e^4}{2\hbar^2}, \tag{5}$$

$$z_n = \frac{x}{nx_0}, \quad x_0 = \frac{\hbar^2}{2mZe^2}, \tag{6}$$

one obtains

$$\left(\frac{d^2}{dz_n^2} + \frac{n}{z_n} - \frac{1}{4} \right)\psi_n = 0. \tag{7}$$

Observe that the helium-surface ''Rydberg'' and ''Bohr radius'' have values

$$\mathcal{E}_0 = Z^2 R_\infty = 0.658086 \text{ meV} = 159.123 \text{ GHz}, \tag{8}$$

$$b_0 = 2x_0 = a_0/Z = 76.01 \text{ Å}. \tag{9}$$

By techniques similar to those used to obtain the solutions for the three-dimensional hydrogen atom, one can obtain the normalized eigensolutions [12,13]

$$\psi_n(z) = [2n^3x_0]^{-1/2}z_n \exp[-z_n/2]L_{n-1}^{(1)}(z_n). \tag{10}$$

This agrees with particular $n=1,2,3$ wave functions in the literature [14].

In Eq. (10) we have used the *generalized* Laguerre polynomials commonly found in the modern mathematical physics literature [15]:

$$L_n^{(\alpha)}(x) = \sum_{k=0}^n \binom{n+\alpha}{n-k}\frac{(-x)^k}{k!} = \frac{e^x x^{-\alpha}}{n!}\frac{d^n}{dx^n}[e^{-x}x^{n+\alpha}]. \tag{11}$$

In Eq. (11), the generalized binomial symbol $\binom{a}{b}$ means $\Gamma(a+1)/[\Gamma(a-b+1)\Gamma(b+1)]$. Also, $L_n^{(0)}(x) = L_n(x)$, where $L_n(x)$ are the ordinary Laguerre polynomials normalized to unity at zero: $L_n(0) = 1$. These polynomials were used instead of the *associated* Laguerre polynomials often defined, for Coulomb wave functions [16], as

$$L_n^j(x) \equiv \frac{d^j\bar{L}_n(x)}{dx^j} = \frac{d^j}{dx^j}\left[e^x \frac{d^n}{dx^n}(e^{-x}x^n) \right]. \tag{12}$$

Here, $\bar{L}_n(x) = (n!)L_n(x)$, the ordinary Laguerre polynomials normalized to $\bar{L}_n(0) = (n!)$. Equation (12) can be confusing, since this definition only holds for integer j. Contrariwise, Eq. (11) is defined for arbitrary α. (This will be very important in the following.) When $\alpha = j$, an integer, the connection between the two forms is

$$L_{n+j}^j(x) = (-1)^j[(n+j)!]L_n^{(j)}(x). \tag{13}$$

The experiments obtain transition energies from excited states to the ground state:

$$\Delta_n = |E_1| - |E_n| = \mathcal{E}_0\left(1 - \frac{1}{n^2} \right). \tag{14}$$

However, the experiments do not yield exact Balmer energies. The Δ_n are all of order 7 GHz too large [6,7]. This is like a quantum defect, since if

*Electronic address: mmn@lanl.gov

$$E_n \to E_{n*} = -\frac{\mathcal{E}_0}{(n*)^2}, \quad n* = n - \delta, \quad (15)$$

then

$$\Delta_{n*} = |E_{1*}| - |E_{n*}| = \mathcal{E}_0 \left(\frac{1}{(1-\delta)^2} - \frac{1}{(n-\delta)^2} \right) \quad (16)$$

$$\approx \mathcal{E}_0 \left[\left(1 - \frac{1}{n^2} \right) + 2\delta \left(1 - \frac{1}{n^3} \right) + 3\delta^2 \left(1 - \frac{1}{n^4} \right) + \ldots \right]. \quad (17)$$

The correction term, $\mathcal{E}_0 \, 2 \, \delta [1-1/n^3]$, varies by only $\sim 10\%$ as n varies from 2 to ∞ [17]. Just fitting the $2* \to 1*$ and $3* \to 1*$ transition energies [8] to this formula yields, $\mathcal{E}_0 = 158.4$ GHz and $\delta = 0.0237$ or an increase in Δ of about 7.8 GHz. In other words, this is like a one-dimensional Rydberg atom.

Elsewhere [18–21], inspired by supersymmetry [22], it was shown how one can obtain exact, analytic, one-particle wave functions for real Rydberg atoms yielding the correct eigenenergies. This also yielded. (a) transition matrix elements in agreement with experiment and complicated many-body calculations [18]; (b) good fine-structure splittings [19]; and (c) Stark splittings whose crossing/anticrossing patterns agree with experiment [20].

The mathematical key to this success is the fact that for proper solutions of the (radial) hydrogen-atom equation one does not really need that $l = $ (integer) and $n = $ (integer). One only needs that $(n-l) = $ (integer), the two separately not having to be integers. That is, the factor $l(l+1)$ in the effective $1/r^2$ potential term need not have l be an integer for a finite-order polynomial radial solution to exist. This is where the $L_n^{(\alpha)}(x)$ become of use [23].

Applying this idea to the present case, we phenomenologically propose for $x > 0$ that $V(x)$ becomes

$$V(x) = -\frac{Ze^2}{x} + \frac{\hbar^2}{2m} \frac{(-\delta)[(-\delta)+1]}{x^2}, \quad x > 0. \quad (18)$$

Then the exact eigenenergies are given by Eq. (15) and the exact wave functions are

$$\psi_{n*}(z) = N_{n*} z_{n*}^{1-\delta} \exp[-z_{n*}/2] L_{n-1}^{(1-2\delta)}(z_{n*}), \quad (19)$$

$$N_{n*} = \left[\frac{1}{2(n*)^2 x_0} \frac{\Gamma(n)}{\Gamma(n+1-2\delta)} \right]^{1/2}, \quad z_{n*} = \frac{x}{n* x_0}. \quad (20)$$

Thus, we have an exact analytic solution to the problem. We can also analytically calculate the expectation values $\langle j* | x^t | k* \rangle$ [24] as double sums of gamma functions [25]. In particular [13],

$$\langle x \rangle_{n*} = x_0 [3n^2 - \delta(6n-1-2\delta)]. \quad (21)$$

When $\delta = 0$ this reduces to the standard result. Also,

$$\langle 1* | x | n* \rangle = \frac{x_0 g^{4-2\delta}}{2} \left(\frac{n*}{1*} \right)^\delta \left[\frac{\Gamma(n+1-2\delta)\Gamma(n)}{\Gamma(2-2\delta)} \right]^{1/2}$$

$$\times \sum_{k=0}^{n-1} \frac{(-g)^k}{k!} \frac{(k+3-2\delta)(k+2-2\delta)}{(n-1-k)},$$

$$g = \frac{2 \cdot 1*}{n* + 1*}. \quad (22)$$

Setting $n*$ to $1*$ in Eqs. (21) and (22), makes them equal.

Unfortunately, this model does not resolve the physical problem of how one realistically cuts off the unphysical, negatively infinite potential at the origin [26]. In fact, this solution makes the problem slightly more difficult: at the origin the potential now goes to negative infinity as $-1/x^2$. If the experimental quantum defect had been of opposite sign, then the added potential would have been positive, like an angular momentum barrier, making the states less bound. This also would have "realistically" modeled the positive work function at the surface of about 1 eV [8].

There are inverse methods for generating inequivalent isospectral Hamiltonians [27–30]. What, in principle, would be an isospectral Hamiltonian with the desired physical properties is one with an added potential that (i) goes, at the origin, to plus infinity at least slightly faster than $[\delta(1-\delta)]/z^2$, (ii) becomes negative for larger z, and (iii) goes to zero at infinity from below.

A first examination of the above inverse methods [27–30] found potentials with the last two properties, but not the first. These potentials go to zero at the origin. An example is [27,30]

$$V_2(z) = \frac{2}{(1*)^2} \left[\left(\frac{2-2\delta}{z_{1*}} - 1 \right) Y + Y^2 \right], \quad x > 0, \quad (23)$$

$$Y = \left[\frac{\exp[-z_{1*}] z_{1*}^{2-2\delta}}{\Gamma(3-2\delta, z_{1*}) - R} \right], \quad (24)$$

where R (which can be chosen to be -2) and $\Gamma(a,z)$ (the incomplete Γ function) are

$$R \equiv \frac{\gamma+1}{\gamma \ (1*) \ N_{1*}^2} = \frac{\gamma+1}{\gamma} \Gamma(3-2\delta),$$

$$\Gamma(a,z) = \int_z^\infty dy \, y^{a-1} e^{-y}, \quad (25)$$

and γ is a dependent constant useful below. Taking units of $x_0 = 1$, the orthonormal eigenfunctions are

$$\chi_{n*}(z) = \psi_{n*}(z) + \int_0^z dy\, K(z,y)\psi_{n*}(y), \quad n > 1, \quad (26)$$

$$K(z,y) = \left(\frac{1}{1*}\right)$$

$$\times \frac{\exp[-z_{1*}/2]\ (z_{1*}^{1-\delta})\exp[-y_{1*}/2]\ (y_{1*}^{1-\delta})}{\Gamma(3-2\delta, z_{1*}) - R}. \quad (27)$$

The exception, with normalization $\gamma/(\gamma+1)$, is

$$\chi_{1*}(z) = \left(\frac{-\Gamma(3-2\delta)}{\gamma^{1/2}}\right)\frac{\psi_{1*}(z)}{\Gamma(3-2\delta, z_{1*}) - R}. \quad (28)$$

There may well be analytic isospectral Hamiltonians with all the desired properties. But to determine their existence requires more investigation.

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$$J_{n,\alpha}^{(\beta)} = \int_0^\infty dt\, \exp[-t]t^{\alpha+\beta}[L_n^{(\alpha)}(t)]^2$$

$$= \frac{\Gamma(n+1+\alpha)}{\Gamma(n+1)}\sum_{j=0}^n \frac{(-1)^{j-n}\Gamma(j+1+\alpha+\beta)}{\Gamma(j+1)\Gamma(j+1+\alpha)\Gamma(n+1-j)}$$

$$\times \frac{\Gamma(j+1+\beta)}{\Gamma(j+1+\beta-n)}. \quad (29)$$

is useful. Note, in particular, that when $\beta = (n-j-1)$ is an integer, then the last Γ function in the denominator cuts off the sum.

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