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, U.S.A.

August 12, 2018

ABSTRACT

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.

PACS: 03.65.Ge, 73.20-r

Email: mmn@lanl.gov
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

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

(1)

\[ = +\infty, \quad x \leq 0, \]  

(2)

where \( \epsilon \) is the dielectric constant [4]. For helium it is [5, 6]

\[ \epsilon = 1.05723, \quad Z = 0.0069547. \]  

(3)

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

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

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

(4)

Making the changes of variables

\[ E_n = -\frac{\mathcal{E}_0}{n^2}, \quad \mathcal{E}_0 = \frac{mZ^2\epsilon^4}{2\hbar^2}, \]  

(5)

\[ z_n = \frac{x}{nx_0}, \quad x_0 = \frac{\hbar^2}{2mZ\epsilon^2}, \]  

(6)

one obtains

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

(7)

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

\[ \mathcal{E}_0 = Z^2R_\infty = 0.658086 \text{ meV} = 159.123 \text{ GHz}, \]  

(8)

\[ b_0 = 2x_0 = a_0/Z = 76.01 \text{ Å}. \]  

(9)

By techniques similar to those used to obtain the solutions for the 3-dimensional hydrogen atom, one can obtain the normalized eigensolutions [12, 13]

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

(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 \([15]\):

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

\[
L_j^{(0)}(x) \equiv \frac{d^j}{dx^j} L_n(x) = \frac{d^j}{dx^j} \left[ e^x \frac{d^n}{dx^n} (e^{-x} x^n) \right].
\] (12)

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

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

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

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

However, the experiments do not yield exact Balmer energies. The \( \Delta_n \) are all of order 7 GHz too large \([3]-[6]\). This is like a quantum defect, since if

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

then

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

\[
\approx \mathcal{E}_0 \left[ \left( 1 - \frac{1}{n^2} \right) + 2\delta \left( 1 - \frac{1}{n^3} \right) + 3\delta^2 \left( 1 - \frac{1}{n^4} \right) + \ldots \right].
\] (17)
The correction term, $E_0 \delta [1 - 1/n^3]$, varies by only $\sim 10\%$ as $n$ varies from 2 to $\infty$ [17]. Just fitting the $2^* \rightarrow 1^*$ and $3^* \rightarrow 1^*$ transition energies [8] to this formula yields, $E_0 = 158.4$ GHz and $\delta = 0.0237$ or an increase in $\Delta$ 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/anti-crossing 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

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

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

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

And

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

Thus, we have an exact analytic solution to the problem. We can also analytically calculate the expectation values $\langle j^*|x^4|k^* \rangle$ [24] as double sums of Gamma functions [25]. In particular [13],

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

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

$$\langle 1^*|x|n^* \rangle = \frac{x_0 \delta^{4-2\delta}}{2} \left( \frac{n^*}{1^*} \right)^\delta \left[ \frac{\Gamma(n+1-2\delta)\Gamma(n)}{\Gamma(2-2\delta)} \right]^{1/2}.$$
\begin{align*}
\times \sum_{k=0}^{n-1} \frac{(-g)^k}{k!} \frac{(k + 3 - 2\delta)(k + 2 - 2\delta)}{(n - 1 - k)}, \quad g = \frac{2 \cdot 1^*}{n^* + 1^*}.
\end{align*}

Setting \( n^* \) to \( 1^* \) in Eqs. (21) and (22), makes then 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 worse: 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 \[27, 30\]

\begin{align*}
V_2(z) &= \frac{2}{(1^*)^2} \left[ \frac{2 - 2\delta}{z_1^*} - 1 \right] Y + Y^2, \quad x > 0, \\
Y &= \frac{\exp(-z_1^*/2) \exp(-y_1^*/2)}{\Gamma(3 - 2\delta, z_1^*) - R},
\end{align*}

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

\begin{align*}
R &\equiv \frac{\gamma + 1}{\gamma (1^*) N_{1^*}^2} = \frac{\gamma + 1}{\gamma} \Gamma(3 - 2\delta), \quad \Gamma(a, z) = \int_{z}^{\infty} dy \ y^{a-1} e^{-y},
\end{align*}

and \( \gamma \) is a dependent constant useful below. Taking units of \( x_0 = 1 \), the orthonormal eigenfunctions are

\begin{align*}
\chi_{n^*}(z) &= \psi_{n^*}(z) + \int_0^z dy \ K(z, y) \psi_{n^*}(y), \quad n > 1, \\
K(z, y) &= \left( \frac{1}{1^*} \right) \frac{\exp(-z_1^*/2) \exp(-y_1^*/2)}{\Gamma(3 - 2\delta, z_1^*) - R}.
\end{align*}
The exception, with normalization $\gamma/(\gamma + 1)$, is

$$
\chi_1^*(z) = \left( \frac{-\Gamma(3 - 2\delta)}{\gamma^{1/2}} \right) \frac{\psi_1^*(z)}{\Gamma(3 - 2\delta, z_1^*)} - R.
$$

(28)

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

Acknowledgements

I wish to thank C. C. Grimes, D. K. Lambert, T. Opatrny, P. L. Richards, L. Spruch, and especially P. M. Platzman for very helpful comments on the physics of electrons on a helium surface. V. A. Kostelecký and P. W. Milonni kindly reviewed a draft. The support of the United States Department of Energy is acknowledged.

References

[1] W. T. Sommer, Stanford University thesis (1964).

[2] M. W. Cole and M. H. Cohen, Phys. Rev. Lett. 23, 1238 (1969); M. W. Cole, Phys. Rev. B 2, 4239 (1970).

[3] V. B. Shilkin, Sov. Phys. JETP 31, 936 (1970) [Zh. Eksp. Teor. Fiz. 58, 1748 (1970)].

[4] L. D. Landau, E. M. Lifshitz, and L. P. Pitaevskii, Electrodynamics of Continuous Media, 2nd Ed. (Butterworth-Heinemann, Oxford, 1984), p. 37, problem 1.

[5] R. F. Harris-Lowe and K. A. Smee, Phys. Rev. A 2, 158 (1970).

[6] T. R. Brown and C. C. Grimes, Phys. Rev. Lett. 29, 1233 (1972); C. C. Grimes, T. R. Brown, M. L. Burns, and C. L. Zipfel, Phys. Rev. B 13, 140 (1976).

[7] D. K. Lambert, Lawrence Berkeley Laboratory report LBL-9553 (1979).

[8] D. K. Lambert and P. L. Richards, Phys. Rev. Lett. 44, (1980); Phys. Rev. B 23, 3282 (1981).
[9] M. W. Cole, in: Two-Dimensional Electron Systems, ed. by E. Y. Andrei (Kluwer, Dordrecht, 1997), p. 1.

[10] P. M. Platzman and M. J. Dykman, Science 284, 1967 (1999).

[11] There is a long and contentious history over the Schrödinger system $V = -e^2/|x|, \ -\infty \leq x \leq +\infty$. The solutions so obtained have very amusing mathematical properties. See, e.g., R. Loudon, Am. J. Phys. 27, 649 (1959); T. D. Imbo and U. P. Sukhatme, Phys. Rev. Lett. 54, 2184 (1985). However, the solutions for this complete-line problem are not physical. See, e.g., U. Oseguera and M. de Llano, J. Math. Phys. 34, 4575 (1993); R. G. Newton, J. Phys. A 27, 4717 (1994); W. Fischer, H. Leschke, and P. Müller, J. Math. Phys. 36, 2313 (1995); and references therein.

[12] M. M. Nieto, Am. J. Phys. 47, 1067 (1979).

[13] To obtain this result, the integral (shown in Ref. [12])

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

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

(29)

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

[14] V. S. Edel’man, Sov. Phys. Usp. 23, 227 (1980) [Usp. Fiz. Nauk 130, 675 (1980)].

[15] W. Magnus, F. Oberhettinger, and R. P. Soni, Formulas and Theorems for the Special Functions of Mathematical Physics, 3rd ed., (Springer, NY, 1966), Sec. 5.5.

[16] L. I. Schiff, Quantum Mechanics, 3rd ed., (McGraw-Hill, NY, 1968), p. 92.

[17] A similar, but much smaller shift, arises from radiative corrections. See R. Shakeshaft and L. Spruch, Phys. Rev. A 22, 811 (1980).

[18] V. A. Kostelecký and M. M. Nieto, Phys. Rev. A 22, 3243 (1985).
[19] V. A. Kostelecký, M. M. Nieto, and D. R. Truax, Phys. Rev. A 38, 4413 (1988).

[20] R. Bluhm and V. A. Kostelecký, Phys. Rev. A 47, 794 (1993).

[21] R. Bluhm and V. A. Kostelecký, Phys. Rev. A 50, 4445 (1994), discusses long-term revival behavior of quantum-defect radial Rydberg wave packets.

[22] V. A. Kostelecký and M. M. Nieto, Phys. Rev. lett. 53, 2285 (1985).

[23] The earliest observation (known to this author) that this type of solution might be useful for quantum-defect theory is in C. Schaefer, *Einführung in die theoretische Physik*, Vol. 3, part 2, (Walter de Gruyter & Co., Berlin, 1937) pp. 142, 286, 298, and elsewhere. Schaefer realized that one could change $l \rightarrow l^*$, and then $n \rightarrow n^*$, to obtain the proper energy levels. However, he was used to the ordinary Coulomb wave functions that use the Laguerre polynomials of Eq. (12) and did not obtain a solution. The first prominent “generalized Kepler” solutions giving the non-integer polynomials was in the classic factorization-method paper of L. Infeld and T. E. Hull, Rev. Mod. Phys. 23, 21 (1951). They, of course, pointed out that one only needs $(n^* - l^*) = \text{integer}$, but no connection was made to quantum-defect theory.

[24] A discussion of photoexcitation and photoejection can be found in R. Shakeshaft and L. Spruch, Phys. Rev. A 31, 1535 (1985). They find that even though angular momentum is not conserved, the transition amplitudes are probably rather good as naively calculated.

[25] H. Buchholz, *The Confluent Hypergeometric Function with Special Emphasis on its Applications* (Springer-Verlag, New York, 1969), Sec. 12.

[26] A flat cut-off is often considered. See, e.g., G. P. Berman, G. Zaslavskii, and A. R. Kolovskii, Sov. Phys. JETP 61, 925 (1985) [Zh. Eksp. Teor. Fiz. 88, 1551 (1985)]; G. F. Saville and J. M. Goodkind, Phys. Rev. A 50, 2059 (1994).

[27] P. B. Abraham and H. E. Moses, Phys. Rev. A 22, 1333 (1980).

[28] M. M. Nieto, Phys. Lett. B 145, 208 (1984).
[29] M. Luban and D. L. Pursey, Phys. Rev. D 33, 431 (1986).

[30] D. L. Pursey, Phys. Rev. D 33, 1048, 3267 (1986).