

## The hydrogen atom as a Morse oscillator

Soo-Y. Lee

Citation: American Journal of Physics **53**, 753 (1985); doi: 10.1119/1.14306 View online: http://dx.doi.org/10.1119/1.14306 View Table of Contents: http://scitation.aip.org/content/aapt/journal/ajp/53/8?ver=pdfcov Published by the American Association of Physics Teachers

Articles you may be interested in Classical motion of a Morse oscillator Am. J. Phys. **46**, 733 (1978); 10.1119/1.11110

Collinear Collisions of an Atom and a Morse Oscillator: An Approximate Semiclassical Approach J. Chem. Phys. **55**, 1522 (1971); 10.1063/1.1676274

Vibrational Excitation in a Morse Oscillator J. Chem. Phys. **53**, 4567 (1970); 10.1063/1.1673988

Semiclassical Transition Probabilities for Collinear Collisions between an Atom and a Morse Oscillator J. Chem. Phys. **51**, 5482 (1969); 10.1063/1.1671975

Thermodynamic Functions of Morse Oscillators J. Chem. Phys. **41**, 1564 (1964); 10.1063/1.1726123



This article is copyrighted as indicated in the article. Reuse of AAPT content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 18.85.28.26 On: Fri, 27 Nov 2015 21:23:51

Le Sage nevertheless carried on an active correspondence with many of the leading scientists of the day, through which his theory became rather widely known. De Luc, for one, accepted it. Saussure and Pictet, while withholding judgment, treated Le Sage's system in their physics lectures at the Academy of Geneva. After Le Sage's death, his pupil and disciple Prevost produced a coherent account of the theory of gravity out of Le Sage's voluminous notes and joined to it a related treatise of his own in his *Deux traités de physique mécanique*. On Le Sage's life, the chief source is Prevost, *Notice de la vie et des écrits de George-Louis Le Sage de Genève* (Geneva, 1805).

<sup>39</sup>P. Prevost, "Mémoire sur l'équilibre du feu," Observations sur la physique, sur l'histoire naturelle, et sur les arts **38**, 314–323 (1791). This periodical, whose publication history is rather complicated, is sometimes cited by the title, Journal de physique.

<sup>40</sup>See Ref. 39, 315, 319. Prevost continued to push his theory in subsequent publications. See, for example, his Recherches physico-mécaniques sur la chaleur (Geneva, 1792), pp. 10-15. A decade later, he attempted to disseminate the theory in Britain by appending a full description of it to his criticism of some of Herschel's experiments on the absorption of radiant heat: P. Prevost, "Quelques remarques sur la chaleur, et sur l'action des corps qui l'interceptent," Philos. Trans. R. Soc. London, 403-447 (1802). (This paper was communicated to the Royal Society for Prevost by Thomas Young.) By 1818, Prevost was able to say that his theory had been accepted by a number of "celebrated physicists." Besides Pictet, he mentioned Biot, William Charles Wells, and René-Just Haüy (Deux traités de physique mécanique, p. 236). Haüy, the distinguished crystallographer, embraced the theory of mobile equilibrium without, however, mentioning Prevost by name in the textbook he wrote for use in the French Lycées: Traité elémentaire de physique (Paris, 1803), Vol. I, p. 118.

 <sup>41</sup>Prevost, Deux traités de physique mécanique, Second Treatise, Book II.
 <sup>42</sup>Rumford, "Historical Review," Collected Works, Vol. I, p. 479; and "Inquiry," Collected Works, Vol. I, pp. 361–362.

<sup>43</sup>Rumford, "Inquiry," Collected Works, Vol. I, pp. 373-374.

<sup>44</sup>See Ref. 43, pp. 361, 414.

<sup>45</sup>See Ref. 43, p. 372.

- <sup>46</sup>See Ref. 43, pp. 421-422.
- <sup>47</sup>Such an explanation might run as follows. Consider first the hot cylinder. This cylinder simultaneously emits and absorbs radiant caloric, but as it is in the act of cooling, it clearly emits more than it absorbs. Blackening the cylinder increases the efficiency of both processes, but increases emission more, as this process was already the dominant one for the hot cylinder. Now, the ball of the thermoscope receives two kinds of

radiant caloric from the direction of the hot cylinder: caloric emitted directly by that cylinder, and caloric emitted originally by the ball of the thermoscope but reflected back at it by the cylinder. Again, blackening the cylinder increases the quantity of the first kind of caloric and diminishes that of the second. But the increase in direct emission by the hot cylinder more than compensates for the decrease in reflection. Consider now the cold cylinder. For this cylinder, which is in the act of warming, absorption is more important than emission. Blackening the cylinder increases the efficiency of both processes, but increases absorption more, since absorption is the predominant process for this cylinder. Thus the quantity of caloric radiated directly by the cold cylinder is increased by blackening, but the quantity of caloric emitted by the ball of the thermoscope and reflected back at it by the cold cylinder is even more strongly decreased. Blackening both cylinders therefore increases the radiant caloric emitted by both, exactly as Rumford noted, but it also decreases the amount reflected by both back towards the thermoscope. The decrease in reflection then compensates for the increase in direct emission.

<sup>48</sup>Rumford, "Inquiry," Collected Works, Vol. I, p. 408.

<sup>49</sup>See Ref. 48, p. 421.

50See Ref. 48, pp. 427-428.

<sup>51</sup>As mentioned above (see Ref. 26), Leslie and Rumford published their studies of radiant heat almost simultaneously. For Rumford, the radiation of cold was one of the crucial phenomena to be explained. For Leslie, it had nowhere near the same importance. Leslie does, however, provide a brief explanation which is a curious blend of emissionist and undulationist ideas. Leslie insists quite strongly that heat is a material substance. In the case of radiation, the substance of heat causes zones of rarefaction in the air. These rarefied zones propagate like waves and carry the heat substance along with them at the speed of sound. In the case of radiant cold, the direction of motion of the substance of heat is opposite to that of the (compressional) aerial pulses. See Leslie, Experimental Inquiry, pp. 241-243. For a comparison of Rumford's and Leslie's ideas on many different aspects of heat, see R. G. Olson, "Count Rumford, Sir John Leslie, and the Study of the Nature and Propagation of Heat at the Beginning of the Nineteenth Century," Ann. Sci. 26, 273-304 (1970)

<sup>53</sup>J. B. J. Fourier, letter to P. Prevost, 22 October 1817. Quoted by Prevost in Exposition élémentaire des principes qui servent de base à la théorie de la chaleur rayonnante, faisant suite à l'ouvrage intitulé Du Calorique rayonnant (Geneva, 1832), pp. 86–93.

<sup>54</sup>Pictet, Essai sur le feu, Sec. 67.

# The hydrogen atom as a Morse oscillator

#### Soo-Y. Lee

Faculty of Science, National University of Singapore, Kent Ridge, Singapore 0511 Singapore

(Received 24 February 1984; accepted for publication 24 July 1984)

In its radial motion, the electron in the hydrogen atom can be pictured as oscillating about the Bohr orbits under Morse potentials. For each principal quantum number n, there corresponds a Morse oscillator with n bound states—one for each allowed value of the angular momentum quantum number l. The equilibrium positions of the Morse oscillators are exactly the Bohr orbits.

## I. INTRODUCTION

The hydrogen atom inspired the beginnings of quantum mechanics. It is simple in structure—consisting of just a proton and an electron; and, to this day, it continues to be used as a test of the predictions of quantum mechanics. It occupies an important position in both the physics and chemistry curricula—in the early part of the course it is introduced as the Bohr atom,<sup>1-3</sup> and later as the Coulomb problem in nonrelativistic quantum mechanics.<sup>4-6</sup> How-

<sup>&</sup>lt;sup>52</sup>Bibliothèque britannique 25, pp. 185–221, 273–311 (1804).

ever, there is little parallel between the Bohr atom and the quantum mechanical (q.m.) Coulomb problem. The Bohr orbits that are central to the planetary Bohr atom have lost their significance, and do not appear explicitly in the q.m. Coulomb problem. The Bohr orbits can only be recovered as the maxima of the radial distribution functions of the 1s, 2p, 3d, etc. orbitals. This all seems very well from the point of view of the Heisenberg uncertainty principle. However, the secondary importance of the Bohr orbits in the q.m. Coulomb problem is an anticlimax to the planetary Bohr model.

This article presents another viewpoint. We reexamine the radial equation of the q.m. Coulomb problem and restore the status of the Bohr orbits. In a sense, we arrive at a quantum mechanical description that is as close in spirit to the planetary Bohr atom as we can get, without violating the Heisenberg uncertainty principle. This has certain advantages, not the least of which is that some classical mechanics can creep into the interpretation of the quantum mechanical (radial) equation.

We obtain a new picture of the one-electron atom, where the electron oscillates about the Bohr orbits subject to Morse potentials.<sup>7-9</sup> For each principal quantum number n, there corresponds a Morse oscillator with n bound states—one for each allowed value of the angular momentum quantum number l, which has integral values  $0 \le l \le n - 1$ . Each Morse potential is a function of a vibration coordinate  $x [ = -\ln(r/r_n^0) ]$ , which is a measure of the radial coordinate r of the electron relative to the radius of the Bohr orbit  $r_n^0$ . The minimum of the Morse potential lies at the Bohr orbit x = 0. The dissociation "energy" of the *n*th Morse oscillator turns out to be the square of the classical angular momentum  $L^2 = n^2 \hbar^2$  of the electron in the Bohr orbit.

In Sec. II we transform the radial equation to a Schrödinger equation for a Morse oscillator. We then compare this with the known solutions for a Morse oscillator in Sec. III to obtain the eigenfunctions and eigenvalues. Then in Sec. IV we discuss the orthogonality of the radial wave functions.

### II. SCHRÖDINGER EQUATION FOR THE ONE-ELECTRON ATOM/ION

In spherical polar coordinates, the Schrödinger equation for the one-electron atom/ion is

$$\frac{1}{r^{2}}\frac{\partial}{\partial r}\left(r^{2}\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^{2}}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^{2}\theta}\frac{\partial^{2}\psi}{\partial\phi^{2}}\right] + \frac{2\mu}{\hbar^{2}}\left(E + \frac{Zq_{e}^{2}}{4\pi\epsilon_{0}r}\right) \quad \psi = 0, \quad (2.1)$$

where  $\mu$  is the reduced mass of the electron,  $-q_e$  is the electronic charge,  $Zq_e$  is the nuclear charge, and  $\epsilon_0$  is the permittivity of vacuum. By expressing the total wave function as a product of a radial wave function R(r) and the (angular) spherical harmonic function  $Y_{lm}(\theta, \phi)$ ,

$$\psi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi), \qquad (2.2)$$

we can separate Eq. (2.1) into two standard equations,

$$\hat{l}^{2}Y_{lm} = \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^{2}\theta}\frac{\partial^{2}}{\partial\phi^{2}}\right]Y_{lm}$$

$$= l(l+1)Y_{lm}, \qquad (2.3)$$

$$-\frac{\hbar^{2}}{2\mu}\frac{1}{r^{2}}\frac{d}{dr}\left(r^{2}\frac{dR}{dr}\right) + \left(\frac{\hbar^{2}}{2\mu}\frac{l(l+1)}{r^{2}}\right)$$

$$-\frac{Zq_{e}^{2}}{4\pi\epsilon_{0}r}R = ER. \qquad (2.4)$$

Equation (2.3) describes the rotational motion of the electron, and can be further separated into a  $\theta$  – and  $\phi$  – equation. The net result is that acceptable solutions of Eq. (2.3) exist only for angular momentum quantum number l that is zero or a positive integer, and  $|m| \leq l$ . The common approach to the radial equation (2.4) is to manipulate it into the form of a well-known equation in mathematical physics—the associated Laguerre equation<sup>10</sup>—and from there to obtain the radial wave functions and eigenenergies.

In this paper, we shall take a different approach to solve the radial equation. First, define a radial wave function u(r)by

$$u(r) = rR(r), \tag{2.5}$$

which upon substitution into Eq. (2.4) yields the following equation for u(r):

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Zq_e^2}{4\pi\epsilon_0 r}\right)u = Eu. \quad (2.6)$$

Next, we define a scaled Langer<sup>11</sup> transformation,

$$r/r^0 = e^{-x},$$
 (2.7)

$$u(r) = e^{-x/2}w(x), (2.8)$$

where  $r^0$  is a constant to be determined later, and the coordinate x, which is dimensionless, measures the relative displacement of the electron from  $r^0$ . Upon substitution into Eq. (2.6) we obtain the following equation for w(x):

$$-\frac{\hbar^2}{2\mu r^{02}}\frac{d^2w}{dx^2} + \left(-Ee^{-2x} - \frac{Zq_e^2}{4\pi\epsilon_0 r^0}e^{-x}\right)w$$
  
=  $-\frac{\hbar^2}{2\mu r^{02}}(l+\frac{1}{2})^2w.$  (2.9)

We now define r<sup>0</sup> as

$$\mathcal{L}^{0} = -Zq_{e}^{2}/2(4\pi\epsilon_{0})E \qquad (2.10)$$

such that Eq. (2.9) has the form of a Schrödinger equation for a Morse potential,

$$-\frac{\hbar^2}{2\mu}\frac{d^2w}{dx^2} + D\left(e^{-2x} - 2e^{-x}\right)w = -\frac{\hbar^2}{2\mu}(l+\frac{1}{2})^2w,$$
(2.11)

where D is defined as

$$D = -Z^2 q_e^4 / 4(4\pi\epsilon_0)^2 E. \qquad (2.12)$$

This is not the regular type of Schrödinger equation where the potential is known, and we seek the eigenvalues. In Eq. (2.11), the unknown eigenenergy E is a parameter in the potential, and the eigenvalues  $-\frac{\pi^2}{(l+\frac{1}{2})^2}/2\mu$  are known.

## **III. MORSE OSCILLATORS**

The solution of the Schrödinger equation for a general Morse potential can be found in Ref. 12; and to save redundancy we shall merely state the results and apply them to our particular Morse potential. It should be noted, through the various transformations above, that if we know the solutions to the Morse oscillator Eq. (2.11), we can obtain the solutions to the radial equation Eq. (2.4), and vice versa.

The Schrödinger equation for a Morse oscillator,

$$-\frac{\hbar^2}{2\mu}\frac{d^2w}{dx^2} + D(e^{-2x} - 2e^{-x})w = \mathscr{C}w, \qquad (3.1)$$

has eigenvalues<sup>12</sup>

$$\mathscr{C}_{k} = -D \left[ 1 - (k + \frac{1}{2})\hbar/(2\mu D)^{1/2} \right]^{2}, \qquad (3.2a)$$

where

$$0 \leq k \leq (2\mu D)^{1/2} / \hbar - \frac{1}{2}$$
 (3.2b)

and eigenfunctions<sup>12</sup>

$$w_k(x) = A y^{\beta} e^{-y/2} {}_1 F_1(a,c;y), \qquad (3.3a)$$

where A is the normalization constant,

$$y = \zeta e^{-x}, \tag{3.3b}$$

$$\zeta = 2\gamma, \tag{3.3c}$$

$$\gamma^2 = 2\mu D / \hbar^2, \qquad (3.3d)$$

$$\beta^2 = -2\mu \mathscr{C}_k / \hbar^2, \qquad (3.3e)$$

 $_{1}F_{1}(a,c;y)$  is the confluent hypergeometric function,<sup>13</sup>

$$a = \beta + \frac{1}{2} - \gamma, \qquad (3.3f)$$

and

$$c = 2\beta + 1. \tag{3.3g}$$

We shall have more to say about the eigenfunctions later, but for now we shall concentrate on the eigenvalues.

Comparing Eq. (2.11) with Eq. (3.1) and using the eigenvalues given in Eq. (3.2a), we obtain

$$-D\left[1-(k+\frac{1}{2})\hbar/(2\mu D)^{1/2}\right]^{2}=-(\hbar^{2}/2\mu)(l+\frac{1}{2})^{2}.$$
(3.4)

The solution of Eq. (3.4) for D yields

$$D = n^2 \hbar^2 / 2\mu, \qquad (3.5a)$$

where there are two possibilities for n,

$$n = k + l + 1 \tag{3.5b}$$

or

$$n = k - l. \tag{3.5c}$$

To obtain the restriction on l for fixed n, we first substitute the expression for D from Eq. (3.5a) into Eq. (3.2b) to obtain

$$0 \leqslant k \leqslant n - \frac{1}{2}, \tag{3.6}$$

but since k must be an integer,

$$0 \leqslant k \leqslant n - 1. \tag{3.6b}$$

Then, using Eq. (3.5b), where l = n - k - 1, we obtain the well-known restriction on l to be

$$0 \leqslant l \leqslant n - 1. \tag{3.7}$$

Eq. (3.5c) can be rejected because it leads to negative integers for *l*, which are forbidden. The discrete energies for the one-electron atom/ion can be obtained by equating Eq. (2.12) to Eq. (3.5a) to give the well-known result

$$E_n = -Z^2 \mu q_e^4 / 2(4\pi\epsilon_0)^2 n^2 \hbar^2.$$
(3.8)

Substituting Eq. (3.5a) into Eq. (2.11), we obtain the result that for each principal quantum number *n* there is one

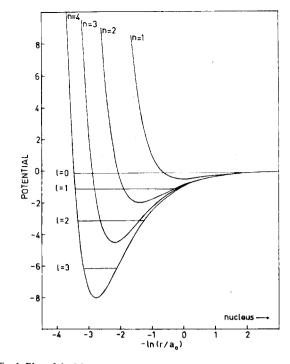


Fig. 1. Plot of the Morse potential  $V(x) = n^2(e^{-2x} - 2e^{-x})$  in units of  $\hbar^2$ , where  $x = -\ln(r/r_n^0) = -\ln(r/n^2a_0)$ , as a function of  $-\ln(r/n^2a_0) = x - 2\ln(n)$ .  $a_0 = 0.529$  Å) is the Bohr radius.

Schrödinger equation,

$$-\hbar^{2}\frac{d^{2}w}{dx^{2}} + n^{2}\hbar^{2}(e^{-2x} - 2e^{-x})w = -\hbar^{2}(l+\frac{1}{2})^{2}w,$$
(3.9)

and one Morse potential,

$$V(x) = n^2 \hbar^2 (e^{-2x} - 2e^{-x}).$$
(3.10)

Equation (3.9) is to be interpreted as the Schrödinger equation for the the centrifugal motion, because the potential [see Eq. (2.9) for a clearer expression] is proportional to the total energy minus the Coulomb energy, which therefore leaves the centrifugal energy. The minimum for the *n*th Morse potential occurs at  $r_n^0$ , where from Eq. (2.10),

$$r_n^0 = -Zq_e^2/2(4\pi\epsilon_0)E_n$$
  
=  $n^2\hbar^2(4\pi\epsilon_0)/Z\mu q_e^2.$  (3.11)

This radius  $r_n^0$  is simply the radius of the *n*th Bohr orbit. Thus Eq. (3.9), which depends on the coordinate x of the relative radial motion about the Bohr orbit, shows that the centrifugal motion is responsible for the oscillations about the Bohr orbits. These oscillations are subject to a Morse potential in the relative coordinate x. It is shown in the Appendix that the "dissociation energy"  $n^2\hbar^2$  for the *n*th Morse potential is the square of the classical angular momentum  $L_n$  of the electron in the Bohr orbit,

$$L_n^2 = n^2 \hbar^2. \tag{3.12}$$

Thus, in the transformed radial equation Eq. (3.9), we have all the parameters of the planetary Bohr atom.

The Morse potentials for various values n = 1, 2, 3, 4 of the principal quantum number, with Z = 1, are plotted in Fig. 1. The allowed angular momentum states are also shown. We obtain the pedagogically pleasing result that the *n*th Morse oscillator has *n* angular momentum states with l = 0, 1, 2, ..., n - 1. For the angular momentum state *l* of the *n*th Morse oscillator, the classical turning points occur at

$$r_{\pm}^{M} = r_{n}^{0} \{ 1 \pm \left[ 1 - (l + \frac{1}{2})^{2} / n^{2} \right]^{1/2} \}.$$
 (3.13)

It is of interest to compare this with the maximum and minimum values of r,

$$r_{\pm}^{BS} = r_n^0 \{ 1 \pm [1 - (l+1)^2/n^2]^{1/2} \}, \qquad (3.14)$$

for the classical Bohr–Sommerfeld orbit<sup>14</sup> with the same quantum numbers n, l. It is easy to show that

$$r_{-}^{M} < r_{-}^{BS} < r_{+}^{BS} < r_{+}^{M} .$$
(3.15)

The major difference is that the precise Bohr orbits occur when l = n - 1 in the Bohr-Sommerfeld theory. This is not the case in the quantum-mechanical Morse picture of the hydrogen atom, because of the uncertainty principle. However, the amplitude of the oscillations about the Bohr orbit is a minimum for l = n - 1. This is the case where the electron has maximum angular momentum, closest to that for the Bohr orbit with principal quantum number n.

It can be seen in Fig. 1 that for a fixed angular momentum quantum number l, the amplitude of the electron oscillation increases with an increase in the principal quantum number n. The amplitude of the oscillation,

$$\Delta r^{m} = 2r_{n}^{0} \left[ 1 - (l + \frac{1}{2})^{2}/n^{2} \right]^{1/2}, \qquad (3.16)$$

can be deduced from Eq. (3.13). A similar trend can be seen for the classical Bohr–Sommerfeld orbits, where from Eq. (3.14),

$$\Delta r^{BS} = 2r_n^0 \left[ 1 - (l+1)^2 / n^2 \right]^{1/2}.$$
(3.17)

As the difference (n - l) increases, the angular momentum of the electron is deviating more and more from the classical angular momentum of the equilibrium Bohr orbit. There will thus be a corresponding increasing deviation of the radial path of the electron from the radius of the Bohr orbit.

#### **IV. THE WAVE FUNCTION**

The wave function w(x) of the transformed radial equation Eq. (2.11) is given by Eq. (3.3),

$$w_{nl}(x) = Ay^{l+1/2}e^{-y/2}F_{1}(l+1-n,2l+2;y), \qquad (4.1)$$

where we have used Eq. (3.5a) for D and  $\mathscr{C} = -\varkappa^2 (l + \frac{1}{2})^2 / 2\mu$  by comparison with Eq. (3.1). The confluent hypergeometric functions in this case are equivalent to the Laguerre polynomials of degree (n - l - 1),

$${}_{1}F_{1}(l+1-n,2l+2;y) = \frac{\Gamma(n-l)\Gamma(2l+2)}{\Gamma(n+l+1)} L^{2l+1}_{n-l-1}(y).$$
(4.2)

The wave functions  $w_{nl}(x)$ , for fixed *n* and variable *l*, of each Morse oscillator are orthonormal to each other,

$$\int_{-\infty}^{\infty} dx \, w_{nl}(x) w_{nl'}(x) = \delta_{ll'}.$$
 (4.3)

Similarly, the wave functions  $u_{nl}(r)$  of Eq. (2.6), for fixed l and variable n, are orthonormal to each other,

$$\int_{0}^{\infty} dr \, u_{nl}(r) u_{n'l}(r) = \delta_{nn'}. \tag{4.4}$$

Translating both Eqs. (4.3) and (4.4) into integrals for the radial wave functions  $R_{nl}(r)$  of Eq. (2.4) and using the relationships expressed in Eqs. (2.5) and (2.8), we obtain the

following orthonormality relations:

$$\int_{0}^{\infty} dr \, R_{nl}(r) R_{nl'}(r) = \delta_{ll'}$$
(4.5)

and

$$\int_{0}^{\infty} dr \, r^{2} R_{nl}(r) R_{n'l}(r) = \delta_{nn'}, \qquad (4.6)$$

respectively. The orthonormality expressed in Eq. (4.6) is well known, based on the fact that the full wave functions  $\psi_{nlm}(r,\theta,\phi)$  and  $\psi_{n'lm}(r,\theta,\phi)$ , where  $n \neq n'$ , of the hermitian Hamiltonian operator correspond to different eigenvalues. Less well known is the orthonormality expressed in Eq. (4.5), which arises from the orthonormality of the wave functions in each Morse oscillator. In summary, there is an orthonormality relation for the radial wave functions with varying principal quantum number *n*, and another for varying angular momentum quantum number *l*. The latter arises from our new viewpoint of the hydrogen atom.

## **V. CONCLUSION**

We commonly associate electronic states with the hydrogen atom, and vibrational states with the Morse oscillator. Electronic energies are typically a hundred times larger compared to vibrational energies, and this would lead us to think that there can be no connection between the electronic motion in a hydrogen atom and the vibrational motion of a diatomic described by a Morse oscillator. There is, however, one similarity between the two. In both cases we are dealing with the relative motion of two particles—in the hydrogen atom it is the motion of an electron about the nucleus, and in a diatomic Morse oscillator it is the relative motion of two nuclei. It should therefore not be surprising that the hydrogen atom can be viewed as an oscillator, with the Bohr orbits as the equilibrium positions.

We have shown the equivalence of the hydrogen atom to a collection of Morse oscillators, where the electron is pictured as oscillating about the Bohr orbits. Knowing the eigenfunctions and eigenvalues of the Morse oscillator enables us to obtain the same for the hydrogen atom, and vice versa. There is an orthonormality relation for the radial wave functions with varying principal quantum number, and another for varying angular momentum quantum number.

### APPENDIX

The classical angular momentum L of an electron of mass  $\mu$  moving in a circular orbit of radius r with velocity v about the nucleus is given by

$$L = \mu vr. \tag{A1}$$

Thus

$$L^{2} = \mu^{2} v^{2} r^{2}$$

$$= 2(\text{Kinetic energy})\mu r^2. \tag{A2}$$

By the virial theorem, applied to the Coulomb potential,

Kinetic energy = - Total energy

$$= -E, \qquad (A3)$$

and thus  $L^2 = -2E\mu r^2.$  (A4)

In the nth Bohr orbit, the classical angular momentum is

thus related to the principal quantum number n,

$$L_n^2 = -2E_n \mu r_n^{02}$$
  
=  $n^2 \hbar^2$ , (A5)

where we have used Eqs. (3.8) and (3.11) for  $E_n$  and  $r_n^0$ , respectively.

- <sup>1</sup>E. H. Wichmann, *Quantum Physics*, Berkeley Physics Course, Vol. 4 (McGraw-Hill, New York, 1967), p. 35.
- <sup>2</sup>M. Karplus and R. N. Porter, *Atoms and Molecules* (Benjamin, Menlo Park, CA, 1970), p. 20.
- <sup>3</sup>T. T. Taylor, *Mechanics: Classical and Quantum* (Pergamon, Oxford, 1976), p. 129.
- <sup>4</sup>Reference 2, p. 104.
- <sup>5</sup>Reference 3, p. 290.

- <sup>6</sup>L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Pergamon, Oxford, 1977), 3rd ed.
- <sup>7</sup>P. M. Morse, Phys. Rev. 34, 57 (1929).
- <sup>8</sup>A. Messiah, *Quantum Mechanics*, translated by J. Potter (North-Holland, Amsterdam, 1962), Vol. 2, pp. 797 and 800.
- <sup>9</sup>G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950), 2nd ed., p. 101.
- <sup>10</sup>H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand, Princeton, NJ, 1956), 2nd ed., p. 128.
- <sup>11</sup>R. E. Langer, Phys. Rev. 51, 669 (1937).
- <sup>12</sup>S. Flugge, *Practical Quantum Mechanics* (Springer-Verlag, New York, 1974), p. 182.
- <sup>13</sup>P. Dennery and A. Krzywicki, *Mathematics for Physicists* (Harper and Row, New York, 1967), p. 316.
- <sup>14</sup>N. Tralli and F. R. Pomilla, Atomic Theory. An Introduction to Wave Mechanics (McGraw-Hill, New York, 1969), pp. 25-31.

## Stark effect in a one-dimensional model atom

Francisco M. Fernández and Eduardo A. Castro<sup>a)</sup> INIFTA, División Química Teórica, Sucursal 4, Casilla de Correeo 16, La Plata 1900, Argentina

(Received 19 September 1983; accepted for publication 20 June 1984)

A very simple one-dimensional, quantum-mechanical analog of the second-order Stark effect in hydrogen is proposed. Its only resonance is found to be a complex root of an algebraic relation among the Airy functions and their derivatives. The Rayleigh–Schrödinger perturbation series is shown to arise from the real part of the resonance. The nonperturbative nature of the resonance width is stressed.

## I. INTRODUCTION

The discrete spectrum of a hydrogen atom is completely destroyed when it is placed in a uniform electric field because the interaction makes the total potential unbounded from below at very large distances from the nucleus. The bound states are shifted into quasibound states (resonances) embedded in the continuum spectrum. The larger the field intensity, the smaller the lifetime of the resonances which are decaying states. If the field strength is small enough, the resonances will lie very close to the bound states of the isolated atom.

Every resonant energy is represented by a complex eigenvalue  $E = \operatorname{Re} E + i \operatorname{Im} E$ , where  $\operatorname{Re} E$  and  $\Gamma = -2 \operatorname{Im} E$  are the position and width of the resonance, respectively. As the field strength tends to zero, the real part approaches an eigenvalue of the isolated atom and the width vanishes exponentially.

The Rayleigh–Schrödinger perturbation theory (RSPT) was the first approximate method used to calculate the resonances of the Stark effect in hydrogen.<sup>1</sup> The interaction potential is considered to be a perturbation and the real part of the resonances are expanded in powers of the field intensity.<sup>1</sup> These RSPT series are known to be divergent and the asymptotic form of their coefficients can be easily calculated.<sup>2</sup>

Some textbooks on quantum mechanics give an appro-

priate description of the main features of the Stark effect in hydrogen.<sup>3</sup> However, the amount of mathematical work required by the simplest approximate calculation of the resonances is so great that the subject is often avoided in introductory courses on quantum mechanics even though it would be really helpful and most probably fascinating for students.

The purpose of this paper is to illustrate the main features of the Stark resonant states by means of a very simple one-dimensional, quantum-mechanical model. Though it is an oversimplified model for the actual Stark effect in hydrogen atoms, the resonances for both problems share some of their main features. Besides, the Schrödinger equation for the model is easily solved and its only resonance is obtained as a complex root of a simple aglebraic equation as shown in Sec. II. The RSPT series in powers of the field strength for the real part of this resonance resembles the one originated in the low-lying resonance of the Stark effect in hydrogen.<sup>1,2</sup> An asymptotic expression for the resonance width is obtained that is valid for small enough field strengths. The nonperturbative nature of  $\Gamma$  is made clear as well as the fact that the RSPT series comes entirely from the real part of the resonance. This is, in our opinion, one of the features of the perturbative approach to resonances that most puzzles students. The RSPT is applied to the model in Sec. III. To this end a method is used which enables us to avoid summations over intermediate states. In

This article is copyrighted as indicated in the article. Reuse of AAPT content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 18.85.28.26 On: Fri, 27 Nov 2015 21:23:51