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Some reflections on the role of semi-classical atomic models in the teaching and learning of introductory quantum mechanics

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The role of "semi-classical" (Bohr–Sommerfeld) and "semi-quantum-mechanical" (atomic orbital) models in the context of the teaching of atomic theory is considered. It is suggested that an appropriate treatment of such models can serve as a useful adjunct to quantum mechanical study of atomic systems. © *2016 American Association of Physics Teachers.*
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I. INTRODUCTION

Semi-classical models of the atom usually get scant attention in the curriculum for most courses on introductory quantum mechanics. This is hardly surprising given that a mere ten years separated the introduction by Sommerfeld of the idea of quantized elliptical orbits[1] (the "old" quantum theory) and the first publication of the Schrödinger equation.[2] Understandably most teachers like to proceed to the "correct" theory at the earliest opportunity. Nevertheless, semi-classical models form part of the visualization framework of the full quantum mechanical treatment of atomic systems. A careful treatment of semi-classical models can assist learners in coming to terms with some of the aspects of quantum theory that may initially appear strange or exotic to the beginner, particularly where the correspondence between old quantization states and those predicted by Schrödinger theory is concerned. Furthermore, even today, old quantization techniques continue to be usefully applied in a number of active research fields; for example, in approximation methods used in the analysis of bound systems where exact analytical solutions to the Schrödinger equation are impossible,[3] or in the recollision electron model that serves as the basis for the generation of attosecond pulses from lasers.[4]

II. GENERAL ELLIPTICAL ORBITS

In both the classical (Kepler) and semi-classical (Bohr–Sommerfeld) central force problems, initial conditions require that the motion of the particle be confined to a plane (note that this is already incompatible with the uncertainty principle) and the problem can be represented by the two plane polar coordinates r and ϕ. The Hamiltonian can thus be written as

$$H = T + V = \frac{p^2}{2m_e} + U(r) = \frac{p_r^2}{2m_e} + \frac{L^2}{2m_e r^2} + U(r) = E, \tag{1}$$

where m_e is the (reduced) mass of the particle and E and L are the respective energy and angular momentum of the system (p_r being the radial momentum). In the case of a potential $U(r) = -\kappa/r$, with κ being a constant ($\kappa = Ze^2/4\pi\epsilon_0$ for a single electron atom), the particle moves on an elliptical orbit, the semi-major and semi-minor axes (a and b) and eccentricity (e) of which are related to the energy and angular momentum via

$$a = \frac{\kappa}{2|E|}, \quad b = \sqrt{\frac{L^2}{2m_e|E|}}, \tag{2}$$

and

$$e = \sqrt{1 - \frac{b^2}{a^2}} = \sqrt{1 + \frac{2L^2E}{m_e\kappa^2}}, \tag{3}$$

while conversely

$$E = \frac{\kappa}{2a} \quad \text{and} \quad L^2 = m_e\kappa\frac{b^2}{a}. \tag{4}$$

As well as energy and angular momentum, a third conserved quantity of this system is the Runge-Lenz vector $\mathbf{A} = (\mathbf{p} \times \mathbf{L})/m_e - \kappa\,\hat{\mathbf{r}}$. The square modulus of this quantity can be written as[5]

$$|\mathbf{A}|^2 = \kappa^2 - \frac{2|E|L^2}{m_e} = \kappa^2\left(1 - \frac{b^2}{a^2}\right), \tag{5}$$

so that

$$|\mathbf{A}| = e\kappa. \tag{6}$$

The vector $\mathbf{e} = \mathbf{A}/\kappa$ is often defined as the "eccentricity vector."

Since the mean radius of a particle in an elliptical orbit is the same as the semi-major axis, we see that the average value of the potential energy is given by $\langle U\rangle = -\kappa/a = 2E$. Thus, using the virial theorem, the average kinetic energy is given by

$$\langle T\rangle = -\frac{\kappa}{2a} = |E|. \tag{7}$$

Finally, the average value of the rotational portion of the kinetic energy is

$$\langle T_{\text{rot}}\rangle = \left\langle \frac{L^2}{2m_e r^2}\right\rangle = \frac{L^2}{2m_e\langle r^2\rangle} = \frac{L^2}{2m_e a^2} = \frac{b^2}{a^2}|E|. \tag{8}$$

III. QUANTIZATION OF THE ORBITS: THE BOHR–SOMMERFELD MODEL

Over a short period of time in 1915 and 1916, the very early quantum ideas of Planck, Bohr, and others were generalized

by Wilson,[6] Ishiwara,[7] and Sommerfeld.[1] Albeit in slightly different forms, these three authors independently proposed a general quantization principle—called the *phase integral* by Sommerfeld—which became the basis of the "old quantum theory" that continued until the development of formal quantum mechanics in the mid 1920s. The quantization principle was cast in the language of phase space and classical Hamiltonian mechanics and essentially stated that, for each degree of freedom k of a system, we have

$$\oint p_k\, dq_k = n_k h, \tag{9}$$

where p_k is the generalized momentum corresponding to the generalized canonical coordinate q_k, n_k is an integer, and h is the Planck constant. In the context of elliptical orbits, the q_k's are the radial and angular coordinates r and θ while the corresponding generalized momenta are radial momentum and angular momentum, respectively. Equation (9) thus leads to

$$\oint L\, d\phi = n_\phi h, \tag{10}$$

and

$$\oint p_r\, dr = n_r h, \tag{11}$$

where n_ϕ (n in Sommerfeld's treatment) and n_r (n' in Sommerfeld) are positive constants. (In a recent paper,[8] it has been shown that these Eqs. (10) and (11) also follow directly from the de Broglie hypothesis.) The quantum numbers n_ϕ and n_r are related to the nowadays more familiar energy and orbital angular momentum quantum numbers n and m by

$$n = n_\phi + n_r \quad \text{and} \quad m = \pm n_\phi. \tag{12}$$

Using this approach, it can be shown[8] that for $1/r$-type potentials the only allowed orbits are those with a quantized eccentricity given by

$$e_{nm} = \sqrt{1 - \frac{m^2}{n^2}}, \tag{13}$$

where n and m are integers such that $n > 0$ and $-n < m < n$. Figure 1 shows the quantized orbits for the case of $n = 4$.

In addition to the eccentricity, other physical quantities are quantized as well, such as the energy

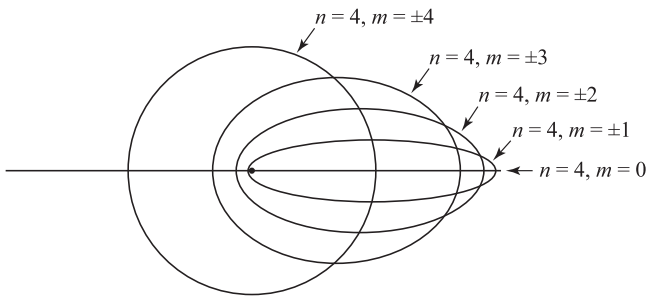

Fig. 1. Sommerfeld atomic orbits for case $n = 4$ with the zero angular momentum ($m = 0$) case included. Note that the $m = 0$ case is twice as long as an ellipse with eccentricity $e = 1$; see the text for details.

$$E_n = -\frac{m_e \kappa^2}{2\hbar^2}\frac{1}{n^2} \equiv \frac{E_0}{n^2}, \tag{14}$$

the angular momentum $L_m = m\hbar$, the magnitude of the Runge-Lenz vector $A_{nm} = e_{nm}\kappa$, and the semi-major and semi-minor axes $a_n = (\hbar^2/m_e\kappa)n^2$ and $b_{nm} = (m/n)a_n = (\hbar^2/m_e\kappa)mn$. Note that in this model, the ground state of the one-electron atom is a triplet state ($n = 1$, $m = 0, \pm 1$). Note also that $m = \pm n$ has $e_{nm} = 0$, which corresponds to the case of circular (Bohr) orbits.

Finally, the average values of the kinetic and potential energies are $\langle T\rangle_n = |E_n| = E_0/n^2$ and $\langle U\rangle_n = 2|E_n| = 2E_0/n^2$, and the mean value of the rotational kinetic energy is

$$\langle T_{\text{rot}}\rangle_{nm} = \frac{m^2}{n^2}|E_n|. \tag{15}$$

A. Note on zero angular momentum states

Despite the above analysis, it is notable that $m = 0$ states are usually excluded in textbook treatments of the Bohr–Sommerfeld atom. A detailed search by this author failed to find a single figure illustrating a zero angular momentum state in any widely used textbook on atomic physics, nor was it possible to find this state indicated in the vast majority of internet images of the Bohr–Sommerfeld atom.

In his 1915 paper,[6] Wilson explicitly states that possible values of the integers n_k in Eq. (9) should include zero but he does not mention the possibility of elliptical orbits. Sommerfeld,[1] on the other hand, argues that while n_r can be zero (in that case denoting a circular orbit), $n_\phi = 0$ corresponds to "the degeneracy of the ellipse area into a twofold straight line. Such a trajectory is on the one hand geometrically impossible, because it would quasi pass through the nucleus, and on the other hand also dynamically forbidden, since the velocity would have to become infinitely large." Thus, Sommerfeld declares that such trajectories must be considered to be "unreal" (*unwirklich*). Sommerfeld repeats this argument in a little more detail in his book *Atombau und Spektrallinien* (1919).[9] There, in a footnote, he points out that if an electron is released from rest and "let fall into the nucleus, then if we suppose that the nucleus to be penetrable, the electron could oscillate pendulum-like to equal distance on the other side, moving to and fro." Nevertheless he immediately proceeds to assert that such an orbit is "to be rejected."

In the intervening years, it became clear that Sommerfeld's argument against the inclusion of the $m = 0$ state could not be sustained. Indeed, a detailed analysis of the "pendulum" states was given by Lindsay[10] as early as 1927 that generally supported Wilson's view. Lindsay also discussed the issue in the context of Schrödinger quantum mechanics, and in the intervening years, it has been accepted that zero angular momentum states should be included in any treatment of the one-electron atom using "old quantization" and should be incorporated in illustrations of the Bohr–Sommerfeld atom as in Fig. 1. For a good recent discussion on the modern view of the old quantum theory including some current applications see Garon *et al.*[3] It is a measure of the influence of Sommerfeld, however, that zero angular momentum states continue to be ignored in textbooks a century later. This can generate misconceptions on the part of learners who may, as a result, associate such states only with the full quantum mechanical theory of the

one-electron atom based on solving the Schrödinger equation.

Since the energy of the state depends on the length of the major axis only, one might expect that the $m=0$ state would be a degenerate ellipse of that length. The fact that the path of the motion is on a line of twice that length might seem surprising at first glance. The explanation lies in what happens when a charged particle travelling in an elliptical orbit penetrates a spherical distribution of charge (it had been known that an atomic nucleus was of finite size since the experiments of Geiger and Marsden[11] in 1909). The net effect is to rotate the axis of the ellipse through some angle θ and, in the case of a particle heading directly towards the centre of the sphere, $\theta=\pi$. Thus, the zero angular momentum state in Fig. 1 can be understood as a degenerate ellipse with the same major axis length as the other states of the same energy but which is rotated through 180° each time the electron passes through the nucleus.

B. Connection with the full quantum mechanical model

The inclusion of $m=0$ states in the Bohr–Sommerfeld atom helps to reveal the details of the connection with the full (Schrödinger) quantum mechanical treatment of the one-electron atom. In the latter model, of course, the electron can no longer be considered to be confined to a plane and the state of the system is described by three quantum numbers (n, l, and m). The integers n and m have effectively the same meaning as in the Bohr–Sommerfeld analysis while the quantum number l is associated with the operator L^2. There is now clearly a direct correspondence between the m states in each model but with one important exception. Since the Schrödinger model requires that $-l<m<l$ and $0<l\leq(n-1)$, there can be no $m=\pm n$ states (corresponding to Bohr–Sommerfeld *circular orbits*) in the full quantum mechanical treatment.

IV. ATOMIC ORBITALS

Atomic orbital theory can be considered as another example of a model situated between the classical and quantum regimes. In this case, however, a classical visualization is superimposed on accepted quantum mechanical results (hence "semi-quantum-mechanical" rather than "semi-classical"). Quantum mechanical probability densities and probability fluxes are adopted and used to generate corresponding charge densities (e.g., "electron cloud") and current densities. Strictly speaking, such models are not compatible with quantum mechanics; nevertheless, orbitals can be interpreted as realistic entities[12] understood to be valid only within the constraints of the model. It is considered that orbitals and orbital diagrams have significant advantages from a pedagogical viewpoint compared to other approaches,[13] particularly for problem solving and visualization.

In the case of the single electron atom considered above, an orbital corresponds to a stationary state of the system. For example, for a $|nlm\rangle$ state (electron spin can be ignored for the purposes of this discussion) the charge density distribution is given by

$$\rho_q(\mathbf{r}) = -e\psi^*_{nlm}\psi_{nlm}, \tag{16}$$

where ψ_{nlm} is the (normalized) time independent wavefunction of that state. While of little relevance to the study of chemistry or condensed matter physics, it is pedagogically instructive to realize that the electron mass is also distributed with the same probability as the charge. Thus the (mass) density in a $|nlm\rangle$ state is given by

$$\rho_M(\mathbf{r}) = m_e\psi^*_{nlm}\psi_{nlm}. \tag{17}$$

Such electronic states are, of course, eigenstates of the Hamiltonian and quantum mechanics disallows any discussion of the time evolution of the system. For the orbital model, however, this restriction can be relaxed to some extent. For example, the angular momentum of the mass cloud about some arbitrary z-axis may be determined as follows:

$$L_z = \int [\mathbf{r}\times\mathbf{v}(\mathbf{r})]_z\, dM, \tag{18}$$

where is $dM=\rho_M(\mathbf{r})d^3\mathbf{r}$ is the element of mass at $\mathbf{r}$. Thus,

$$L_z = \int [\mathbf{r}\times\mathbf{v}(\mathbf{r})\rho_M(\mathbf{r})]_z\, d^3\mathbf{r} = \int [\mathbf{r}\times\mathbf{J}_M(\mathbf{r})]_z\, d^3\mathbf{r}, \tag{19}$$

where is $\mathbf{J}_M(\mathbf{r})$ is the mass current density (electron mass times the probability flux), given by

$$\mathbf{J}_M(\mathbf{r}) = \frac{\hbar}{2i}\left[\psi^*_{nlm}\nabla\psi_{nlm} - \psi_{nlm}\nabla\psi^*_{nlm}\right]. \tag{20}$$

Using

$$\nabla\psi = \frac{\partial\psi}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial\psi}{\partial\theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{\partial\psi}{\partial\phi}\hat{\boldsymbol{\phi}}, \tag{21}$$

gives

$$\mathbf{J}_M(\mathbf{r}) = \frac{m\hbar}{r\sin\theta}|\psi_{nlm}|^2\hat{\boldsymbol{\phi}}, \tag{22}$$

from which one gets

$$\mathbf{L} = -\int[\mathbf{r}\times\mathbf{J}_M(\mathbf{r})\, d^3\mathbf{r}]\hat{\boldsymbol{\theta}}, \tag{23}$$

and

$$L_z = \int [\mathbf{r}\times\mathbf{J}_M(\mathbf{r})]_z\, d^3\mathbf{r} = m\hbar\int|\psi_{nlm}|^2\, d^3\mathbf{r} = m\hbar, \tag{24}$$

as expected from a full quantum mechanical treatment. However, in this case, the result is interpreted as arising from the rotation of the orbital.

In this interpretation, the angular momentum of the mass element has a component in the azimuthal plane; this does not give rise to a conserved quantity, however, as it is continuously changing direction and integrates to zero. Similarly, the Runge-Lenz vector, while lying in the azimuthal plane, is not fixed in space as it is in the classical model. The square of this quantity, however, remains a conserved quantity given by

$$|\boldsymbol{A}|^2 = \kappa^2\left[1 - \frac{l(l+1)}{n^2}\right]. \tag{25}$$

In this context, the fact that the wavefunctions are eigenstates of the operator $L^2=(\kappa^2 I - A^2)m_e/2|E|$ can be seen to arise from the conservation of the Runge-Lenz vector.

Using similar considerations, one can attempt to determine the rotational kinetic energy

$$T_{\text{rot}} = \int \frac{1}{2}|\mathbf{v}(\mathbf{r})|^2\, dM = \frac{1}{2}\int \rho_M(\mathbf{r})|\mathbf{v}(\mathbf{r})|^2\, d^3\mathbf{r}$$
$$= \frac{1}{2}\int \frac{|\mathbf{J}_M(\mathbf{r})|^2}{\rho_M(\mathbf{r})}\, d^3\mathbf{r} = \frac{1}{2}\frac{m^2\hbar^2}{m_e}\int \frac{1}{r^2\sin^2\theta}|\psi_{nlm}|^2\, d^3\mathbf{r}$$
$$= \frac{m}{n}|E_n|. \tag{26}$$

Note, however, that this result differs from a full quantum mechanical determination of the average rotational kinetic energy of the system in the $|nlm\rangle$ state since, in the latter case,

$$\langle T_{\text{rot}}\rangle_{nml} = \left\langle \frac{L^2}{2m_e r^2}\right\rangle_{nml} = \frac{1}{2m_e} l(l+1)\hbar^2 \frac{m_e^2\kappa^2}{\hbar^4 n^3\left(l+\frac{1}{2}\right)}$$
$$= \frac{l(l+1)}{\left(l+\frac{1}{2}\right)n}|E_n|. \tag{27}$$

Note that for $l \gg 1$, we have $\langle T_{\text{rot}}\rangle_{nlm} \approx (l/n)|E_n| = (l/n)\langle T\rangle_{nlm}$ instead of $(m/n)|E_n|$ as given in Eq. (26). Nevertheless, for $n \approx l \approx m \gg 1$, we have $\langle T_{\text{rot}}\rangle_{nlm} = \langle T\rangle_{nlm}$, so that all of the kinetic energy is associated with rotation, as in the case of circular motion in a planetary model. This is to be expected from the correspondence principle, which requires that quantum probability distributions approach the corresponding classical situation when some appropriate quantum numbers become large.[14]

It can be seen from this discussion that the simple treatment of an atomic electron as a rotating mass/charge cloud suffers from the same drawback as planetary models; namely, only the two quantum numbers n and m are involved. The third quantum number l arises from specifically quantum mechanical considerations. Thus, atomic orbital models, such as employed in chemistry, superimpose the naive model on results obtained from the full quantum mechanical treatment.

A. Connection with the Bohr–Sommerfeld model

Some parallels between the atomic orbital model and the Bohr–Sommerfeld atom can be seen if we consider the case of an orbital where the rotational kinetic energy arises entirely from rotation about the z-axis; in other words,

$$L^2 = L_x^2 + L_y^2 + L_z^2 \to L_z^2 \quad \text{or} \quad l(l+1) \to m^2. \tag{28}$$

In this case,

$$\langle T_{\text{rot}}\rangle_{nml} \to \left\langle \frac{L_z^2}{2m_e r^2}\right\rangle_{nml} = \frac{m^2}{\left(l+\frac{1}{2}\right)n}|E_n|, \tag{29}$$

and when $n \approx l \gg 1$, we get

$$\langle T_{\text{rot}}\rangle_{nml} \to \frac{m^2}{n^2}\frac{E_0}{n^2} = \frac{m^2}{n^2}\langle T\rangle_{nml} = \frac{m^2}{n^2}|E_n|, \tag{30}$$

as was the case for the Bohr–Sommerfeld model [see Eq. (15) above], and, similarly,

$$|\mathbf{A}|_{nlm} \to \kappa\sqrt{1-\frac{m^2}{n^2}}. \tag{31}$$

Despite the connection between the two models outlined here, learners would normally encounter each one at very different points in their study of quantum mechanics. The Bohr–Sommerfeld model naturally lies somewhere between the Bohr atom and introduction of the Schrödinger equation. Prior study of this model would enable students, when later encountering Schrödinger quantum mechanics, to distinguish between those features of purely quantum origin from those that arise from classical or semi-classical considerations. On the other hand, atomic orbital models only make sense after a full quantum mechanical treatment of the one-electron atom has been developed or in the context of courses in which the results of the quantum mechanics of atoms are accepted without proof. Atomic orbital theory provides a basis for the study of more complicated systems, such as multi-electron atoms or molecular theory. At the same time, as mentioned in the introduction, the Bohr–Sommerfeld model can still play a useful role in some current areas of physics.

For some interesting discussions on relationships between Bohr and Bohr–Sommerfeld models and full quantum mechanical treatments of the one-electron atom see Refs. 15–20.

V. CONCLUSIONS

An appropriate treatment of semi-classical atomic models can serve as an insightful underpinning for teaching the application of the Schrödinger equation to atomic systems. It is important, however, that a number of particular issues be borne in mind:

(1) Zero angular momentum states should always be included in any treatment of the Bohr–Sommerfeld atom.
(2) It needs to be made clear that atomic orbital models are not fully compatible with quantum mechanics. In communicating such models, teachers should not be inhibited in using concepts at variance with formal quantum theory, provided that the limits to the application of the model are outlined clearly.
(3) The correspondence and differences between the atomic states predicted by different models (Bohr–Sommerfeld planetary, atomic orbital, and quantum mechanical) should be emphasized.

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Seven-in-One Apparatus

This apparatus was designed by A.P. Gage of the Boston English High School about 1880. This example, in the Greenslade Collection, is by Cenco and dates from the 1940s, although it is in the 1909 Cenco catalogue. The seven experiments are: the Magdeburg hemispheres; the elasticity of air; the hydraulic press; the hydrostatic paradox; the pneumatic lift; equality of fluid pressure in all directions; atmospheric pressure. This cost $16.75 in the 1937 catalogue. (Notes and picture by Thomas B. Greenslade, Jr., Kenyon College)