Classical view of the properties of Rydberg atoms: Application of the correspondence principle

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The properties of Rydberg atoms are contrasted with those of hydrogen atoms using both classical and quantal points of view. It is shown that, classically, the effects of the ionic core of the Rydberg atom produce a precession of the otherwise Keplerian elliptical orbit of the excited electron, and that this precession is responsible for the nonhydrogenic properties. Using the correspondence principle, classical properties are then related to quantum mechanical properties by correlating the precession frequency with the quantum defect δ_l. The linear and quadratic Stark effects are also discussed and it is shown that a negative polarizability of the atom is a consequence of a positive $\partial\delta_l/\partial l$. In the Appendix, the "gravitational defect" associated with the precession of the perihelion of the Keplerian orbit of the planet Mercury is presented.

I. INTRODUCTION

Although the hydrogen atom serves as a convenient starting point for description of physical phenomena involving multielectron atoms, significant differences exist. This is because the favored status of the $1/r$ potential in nature, the special symmetry of this potential, endows the hydrogen atom with unique properties. An example of the inapplicability of hydrogenic properties to multielectron atoms is the weak field Stark effect. If the electric field is high enough to produce energy shifts that are large compared to fine structure splittings, but smaller than the differences between field-free states, the hydrogen atom exhibits a linear Stark effect. Because the accidental degeneracy peculiar to the $1/r$ potential is broken by interelectron repulsion in multielectron atoms, the first-order terms vanish, and the Stark shifts are quadratic in electric field.[1] Of course high-lying singly excited states, frequently referred to as Rydberg states, behave, in many ways, as states of hydrogen atoms. Nevertheless, the small non-Coulombic potential of the ionic core causes the Stark structure of even these highly excited atoms to deviate substantially from that of hydrogen atoms.

In spite of these differences, or in fact because of them, it is instructive to use the hydrogen atom as a standard for comparison. The deviations from hydrogenic behavior can provide insight and thus lead to a fuller understanding of the effects under study, as well as a greater appreciation for the uniqueness of the Coulomb and gravitational potentials. As discussed in an earlier publication[2] (hereafter referred to as I), examination from a classical point of view permits visualization of the effects. We therefore present in this paper a classical picture of some properties of Rydberg atoms, and use the correspondence principle to relate this classical picture to quantal properties.

II. THE QUANTUM DEFECT

For simplicity we consider Rydberg states of "one electron atoms," for example the alkalis, in which excited states are formed by promotion of a single electron outside a closed, or nearly closed, core of $Z-1$ electrons. For hydrogen, the energy levels are given by the Rydberg formula

$$E_n = -1/2n^2, \tag{1}$$

where n is the principal quantum number; atomic units are used throughout. It is found that a formula for the energies of atoms in Rydberg states (Rydberg atoms) can be written in a way that is reminiscent of Eq. (1):[3]

$$E_{n,l} = -1/2(n-\delta_l)^2, \tag{2}$$

where δ_l, the quantum defect, is a function of the angular momentum l of the excited valence electron, the Rydberg electron. While δ_l depends on l, it is virtually independent of n. Thus although Eq. (2) is similar in appearance to the Rydberg formula for hydrogen, it is clear that the accidental degeneracy of hydrogen is broken in the multielectron atoms. Nonetheless, for Rydberg atoms, the energies of all states of a given value of l are obtained from a single value of δ_l; each such set of states is called a Rydberg series and the atoms are therefore referred to as Rydberg atoms.

Those states that are the most nearly hydrogenic will be characterized by very small values of δ_l. This must correspond to states of sufficiently high angular momentum to cause the Rydberg electron to avoid the core, thereby minimizing its effect on the motion. Table I contains a listing of the quantum defects for the first few Rydberg series' of the alkali atoms. It is generally the case that δ_l is small for values of l that are greater than the maximum angular momentum of a core electron[4] l_{core}, as is illustrated in the table. Notice also that a value of $\delta_l > 1$ indicates that the ordering of the l states, as designated by the values of n, has been altered from that of hydrogen.

In addition to the utility of the quantum defect in providing a simple formula for the energy levels, it also represents the shift in phase, as compared to hydrogenic wave func-

Table I. Maximum angular momenta l_{core} and quantum defects δ_l for the alkali atoms. (Adapted from Ref. 3.)

Atom	l_{core}	$l=0$	$l=1$	$l=2$	$l=3$
Li	1	0.40	0.04	0.00	0.00
Na	2	1.35	0.85	0.01	0.00
K	3	2.19	1.71	0.25	0.00
Rb	4	3.13	2.66	1.34	0.01
Cs	5	4.06	3.59	2.46	0.02

tions, of the multielectron wave functions.[5] Thus the designation of the quantum defect by the symbol δ_l is not coincidence. It is, as for unbound systems, the phase shift due to scattering of the electron by the core. This leads to a classical picture of the Rydberg electron executing a nearly Keplerian orbit when far from the core, but having this orbit altered each time it encounters the core.

III. MULTIELECTRON ATOMS IN FIELD-FREE SPACE

The major contribution to δ_l results from deviations to the $1/r$ potential as the electron penetrates the ionic core.[4] For high angular momentum states, however, core penetration becomes vanishingly small, but relativistic effects become important.[4] Since, in this paper, our attention is directed toward a classical depiction of the Rydberg atom, we consider states of relatively low angular momentum, but for which $l > l_{\text{core}}$ (see Table I). For such states, the major contribution to the quantum defect is from polarization of the ionic core by the valence electron.

To examine the consequences of core polarization it is necessary to include in the Hamiltonian the multipole expansion of the potential energy of the core. The two most important terms in this expansion are the induced dipole and induced quadrupole terms. Thus the Hamiltonian can be written

$$H = H_{\text{Coulomb}} - \alpha_d/2r^4 - \alpha_q/2r^6, \tag{3}$$

where H_{Coulomb} is the hydrogen Hamiltonian, α_d and α_q are the dipole and quadrupole polarizabilities, respectively. Note that the potential in this Hamiltonian is still a central potential and total angular momentum is therefore conserved. Thus quantum mechanically l is still a good quantum number; classically the motion of the Rydberg electron is still confined to a plane.

For our conditions $\delta_l \ll n$ and we may approximate Eq. (2) by

$$E_n \approx -1/2n^2 - \delta_l/n^3, \tag{4}$$

so the first-order corrections to the hydrogenic energies are proportional to n^{-3}. Furthermore, using the notation of Freeman and Kleppner[4] and the conditions on l imposed in this paper, we may write δ_l as

$$\delta_l = \delta_{\text{pol}} = \delta^d_{\text{pol}} + \delta^q_{\text{pol}}, \tag{5}$$

where the terms on the right represent the contributions of dipole and quadrupole polarizabilities, respectively.

For classical orbits with these restrictions on l, the non-Coulombic terms in the potential are small because the electron avoids the core. In accordance with Kepler's second law, which applies to any central potential, a major fraction of the orbital "period" is spent at large values of r on a very nearly Keplerian ellipse with period $\tau = 2\pi n^3$, as given by Kepler's third law. We may therefore compute the energy of the Rydberg electron by averaging the Hamiltonian over an orbital period. In this picture, the polarizability leads to the quantum defect. Mathematically the correlation is clear because the average of H_{Coulomb} corresponds to the hydrogenic energy.

We may, using classical orbits, evaluate the individual contributions to δ_l; the average values $\langle r^{-4}\rangle$ and $\langle r^{-6}\rangle$ over a Keplerian orbit are required. We have

$$\langle r^{-m}\rangle = \frac{1}{2\pi n^3}\int_0^{\tau} r^{-m}\,dt. \tag{6}$$

Using plane polar coordinates (r,ϕ), Kepler's second law (conservation of angular momentum) is $r^2\dot{\phi} = l$ and the equation of the elliptical orbit resulting from a pure Coulomb potential is

$$r = l^2/(1 + \epsilon\cos\phi), \tag{7}$$

where ϵ is the eccentricity. Together with $dt = d\phi/\dot{\phi}$ these relationships lead to

$$\langle r^{-m}\rangle = \frac{l^{(3-2m)}}{2\pi n^3}\int_{-\pi}^{\pi}(1 + \epsilon\cos\phi)^{(m-2)}d\phi. \tag{8}$$

Integration of Eq. (8) with $m = 4$ and with $m = 6$ yields

$$\langle r^{-4}\rangle = (l^{-5}/n^3)\left[1 + (\tfrac{1}{2})\epsilon^2\right] \tag{9}$$

and

$$\langle r^{-6}\rangle = (l^{-9}/n^3)\left[1 + 3\epsilon^2 + (\tfrac{3}{8})\epsilon^4\right]. \tag{10}$$

Since both $\langle r^{-4}\rangle$ and $\langle r^{-6}\rangle$ are proportional to n^{-3}, and δ_l is the coefficient of n^{-3} in the equation for the energy, Eq. (4), the contributions of the polarizabilities to δ_l are readily obtained.

Now $\epsilon^2 = (1 - l^2/n^2)$ (See Table I of I) so that Eqs. (9) and (10) may be cast entirely in terms of l and n. Furthermore, since $l^2/n^2 \ll 1$ we may ignore terms higher than first order in l/n. The results are

$$\delta^d_{\text{pol}} = (\tfrac{3}{4})\alpha_d l^{-5} \tag{11}$$

and

$$\delta^q_{\text{pol}} = (\tfrac{35}{16})\alpha_q l^{-9}, \tag{12}$$

which are noteworthy by their strong l dependences. These l dependences illustrate the short-range nature of the polarizability on the mechanics of the classical atom. Interestingly, to the level of approximation used here, these results are identical to those obtained by Freeman and Kleppner[4] using a quantum mechanical formulation and the same level of approximation.

In this classical view of the atom the electron executes a very nearly Keplerian ellipse that is slightly distorted near the core, primarily by dipole polarization of the core. This distortion causes the axis of the ellipse to shift, leading to precession of the orbit about the force center. Under these conditions the Keplerian orbit may itself be treated as a dynamical entity. This is illustrated in Fig. 1 where the trajectory shown was computed using an attractive $1/r^4$ term added to the $1/r$ potential. Note that if the distortion is caused by a repulsive force, then the precession will be in the opposite direction.

There is an obvious analogy between the precession of the elliptical electronic orbits in Rydberg atoms and the well-known advance of the perihelion of the orbit of the planet Mercury.[6] In the gravitational case, however, polarization cannot occur because repulsive forces evidently do not exist. Nonetheless, the mathematics of the two problems is essentially the same, but general relativity requires the addition of a small $1/r^3$ term to the Newtonian gravitational potential.[7] This perturbation causes a deviation from the Keplerian energy that may be described in terms of a "gravitational defect." This defect and the resulting precession of the perihelion of the orbit of Mercury are discussed in more detail in the Appendix.

The rate of precession of the electronic orbit may be ob-

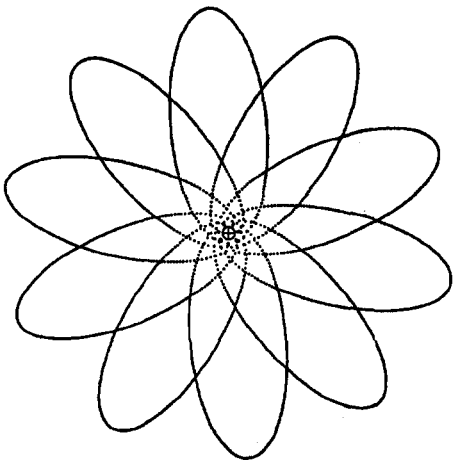

Fig. 1. Precession of a nearly Keplerian elliptical orbit of the Rydberg electron about a positively charged nucleus. The precession is produced by adding a term $-\alpha_d/2r^4$ to the Coulomb potential with $\alpha_d = 40$ a.u.

tained in terms of the quantum defect. To do this we average the time dependence of the Lenz vector **A** as defined in I, over a Keplerian period. We have

$$\dot{\mathbf{A}} = \dot{\mathbf{p}}\times\mathbf{L} + \mathbf{p}\times\dot{\mathbf{L}} - \dot{\mathbf{r}}. \tag{13}$$

Now, for a central potential $\dot{\mathbf{L}} = 0$ and

$$\dot{\mathbf{r}} = [1/r^2]\mathbf{L}\times\hat{\mathbf{r}}. \tag{14}$$

Further, $\dot{\mathbf{p}}$ is the force which is given by $\nabla V(r)$ so that, for a central potential of the form

$$V(r) = -1/r + V'(r), \tag{15}$$

we have

$$\dot{\mathbf{A}} = \frac{1}{r}\frac{dV'}{dr}[\mathbf{L}\times\mathbf{r}]. \tag{16}$$

Now, assuming that the precession is caused by a potential of the form $V'(r) = -\beta r^{-q}$ and that **A** is constant over a single orbital period, we have

$$\dot{\mathbf{A}} = \beta q\mathbf{L}\times\langle\hat{\mathbf{r}}/r^{q+1}\rangle$$
$$= \beta q\langle\cos\phi/r^{q+1}\rangle_t[\mathbf{L}\times\mathbf{A}/|\mathbf{A}|], \tag{17}$$

where the subscript on the average indicates that this is a time average over one Keplerian "period." This time average is most easily computed by converting to an average over ϕ with the help of Kepler's second law, $r^2\dot{\phi} = l$, leading to

$$\left\langle\frac{\cos\phi}{r^{q+1}}\right\rangle_t = \frac{1}{n^3 l}\left\langle\frac{\cos\phi}{r^{q-1}}\right\rangle_\phi.$$

We also make use of the fact that

$$\left[\frac{\cos\phi}{r^{q-1}}\right] = \frac{l^2}{q}\frac{d}{d\epsilon}\left[\frac{1}{r^q}\right] \tag{18}$$

and interchange the order of differentiation and integration. If we assume that the dipole term in Eq. (3) causes the precession, then $\beta = \alpha_d/2$ and $q = 4$, leading to

$$\left\langle\frac{\cos\phi}{r^5}\right\rangle = \frac{l^{-7}}{4n^3}\epsilon[6 + (\tfrac{3}{2})\epsilon^2]. \tag{19}$$

Again ignoring terms in l/n higher than first order we arrive at

$$\dot{\mathbf{A}} = (15/4)(\alpha_d/l^7 n^3)[\mathbf{L}\times\mathbf{A}], \tag{20}$$

which shows that the frequency of precession of the orbit about **L** is given by

$$\omega_c = \frac{15}{4}\frac{\alpha_d}{l^6 n^3} = \frac{5}{n^3 l}\delta_l \tag{21}$$

in units of radians per atomic unit of time. We note that this treatment is equivalent to the use of classical perturbation theory,[8] and that the same result is obtained using that formalism.

Equation (21) shows explicitly the relationship between the quantum defect and the precessional frequency, either of which may be regarded as a consequence of the other. It also shows that the precession rate increases with decreasing l because the effect of the short-range polarization potential on elongated orbits will be greater than the effect on nearly circular orbits.

The relationship between δ_l and ω_c can be clarified by noting that each value of n characterizes a group, or manifold, of states that differ in energy depending on their values of l, and consequently δ_l. According to Eq. (21) these energy differences are associated with the precessional frequencies characteristic of different angular momenta. Thus, according to the correspondence principle, radiation given off in a transition between adjacent l states will be of the same frequency as the precessional frequency ω_c. Since $\hbar = 1$ in atomic units, the radiation frequency ω_{rad} is the energy difference between successive l states as given by Eq. (4). Assuming that the major contribution to δ_l is that of the dipole term, as given by Eq. (11), the correspondence principle leads to

$$\omega_c = \omega_{\text{rad}}$$
$$= (1/n^3)[\delta_l - \delta_{l+1}]. \tag{22}$$

Treating l as a continuous variable and bearing in mind that it is unitless in atomic units we have

$$\omega_c = -\frac{1}{n^3}\frac{\partial\delta_l}{\partial l} = -\omega_n\frac{\partial\delta_l}{\partial l}, \tag{23}$$

where ω_n is the electronic orbital frequency. Applying Eq. (23) to Eq. (11) we see that, indeed, the precession frequency given by Eq. (21) is recovered. Note that it is the rate of change of the quantum defect with angular momentum that governs the precession rate and not the actual value of δ_l.

IV. MULTIELECTRON ATOMS IN AN ELECTRIC FIELD

Using the classical picture of Rydberg atoms, together with the view of the hydrogen atom presented in I, we may now examine the classical picture of a Rydberg atom subjected to an electric field **F**. As discussed in I, application of an electric field causes the elliptical orbit of a hydrogen atom to precess about the field vector. For a Rydberg atom this effect will also occur, as will the precession due to the presence of the ionic core.

Consider first the case in which the electric field is so weak that ω_c is much greater than the frequency of precession caused by the electric field; both frequencies are assumed to be much lower than $\omega_n = 1/n^3$, so that, as usual, the orbit is treated as a dynamical entity. Quantum mechanically this corresponds to Stark shifts in energy that

are smaller than the energy separation between adjacent l states of the same n manifold. Classically, the charge distribution resulting from precession of the orbit about the nucleus will be very nearly symmetric (see Fig. 1). There will then be essentially no energy shift proportional to the first power of F, as there is in hydrogen, because **d**, the time-averaged permanent electric dipole moment, is zero. The field can, however, induce the atom to have a dipole moment by polarizing it. This polarization is not the same as that discussed in Sec. III of this paper; in the present case the entire atom, including the Rydberg electron, is being polarized by the electric field. This induced dipole moment is given by $\alpha\mathbf{F}$, where α is the polarizability of the atom,[3] not to be confused with α_d and α_q, the dipole and quadrupole polarizabilities of the core.

Although there is no first-order shift in the energy for these weak fields, the induced dipole moment contributes an energy

$$E_{\text{Stark}} = -(\tfrac{1}{2})\alpha\mathbf{F}\cdot\mathbf{F} = -(\tfrac{1}{2})\alpha|\mathbf{F}|^2, \tag{24}$$

thus producing a quadratic Stark effect. We therefore see the contrast between the weak field Stark effect in hydrogen and in Rydberg atoms; it is linear in hydrogen and quadratic in Rydberg atoms.

As discussed in I, the first-order Stark effect in hydrogen is caused by the permanent electric dipole moment of the excited states. Classically, the existence of this permanent electric dipole moment is a consequence of the asymmetric charge distribution that results from variation of the orbital electronic speed, as dictated by Kepler's second law. Quantum mechanically, states with permanent electric dipole moments may be constructed by taking an appropriate linear combination of the degenerate angular momentum eigenstates, or, alternatively, by separating the Schrödinger equation in parabolic coordinates.[9-11] Classically, the absence of a first-order Stark effect in multielectron atoms is the result of symmetrization of the charge distribution by precession of the Keplerian ellipse. Quantum mechanically, the first-order effect vanishes because the accidental degeneracy of the hydrogen atom is broken by the presence of the core. Since the non-Coulombic potential of the core is a central potential, the Schrödinger equation can still be separated in spherical coordinates, but no longer in parabolic coordinates. Thus the nondegenerate angular momentum eigenfunctions, the squares of which are symmetric through the force center, cannot have a permanent electric dipole moment. More importantly, since they are nondegenerate, an eigenfunction of the same energy that has an asymmetric charge distribution cannot be constructed. At the heart of the difference between the Stark effects in hydrogen and in multielectron atoms is therefore the broken symmetry of the Coulomb potential.

The classical view of the effect of a weak electric field on the precessing Keplerian orbit provides a clear picture of the nature of the quadratic Stark shift. It is often remarked that the external field polarizes a charge distribution, thus inducing a dipole moment $\mathbf{d} = \alpha\mathbf{F}$. In such a picture the charge distribution will always be polarized in the direction of F so that the resulting Stark shift will be to lower energy [see Eq. (24)]. This is, however, not always the case, as may be illustrated by considering the Stark structure of sodium atoms. Figure 2 is a generic diagram of high-lying energy levels of sodium subjected to a weak electric field. The two groups of states, each emanating from what appears to be a single energy, represent the nearly hydrogenic sets of levels having $l \geqslant 2$, and usually referred to as the hydrogenic manifold. Although the electric field is "weak" insofar as it Stark shifts the isolated p state, it is strong enough to cause states having $l \geqslant 2$ to exhibit linear shifts in energy on the scale of Fig. 2, thus the designation "hydrogenic" manifold. Although the zero-field levels of each manifold appear to be degenerate on the diagram, a result of their small quantum defects, they are not of course truly degenerate as are the levels of pure Coulomb potential. The relatively isolated $(n+1)p$ state undergoes a quadratic Stark shift as shown. Because the quantum defect does not vary appreciably with n, the zero-field location of the p-state energy between adjacent hydrogenic manifolds will always be the same. According to Table I, $\delta_1 = 0.85$ placing it 0.85 of the hydrogenic energy difference, $1/n^3$, below the upper manifold [see Eq. (4)].

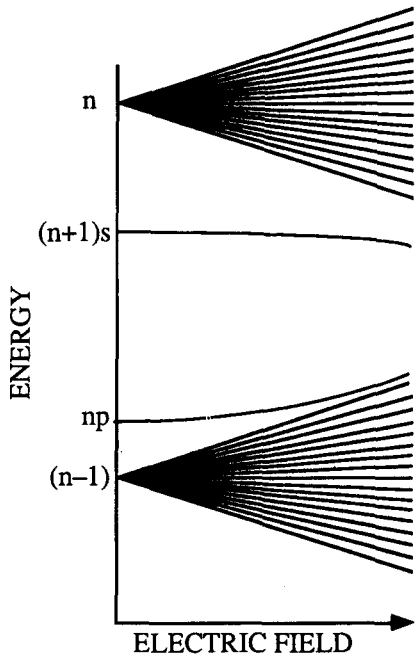

Fig. 2. Generic diagram of the high-lying levels of sodium in a weak electric field. The groups of states labeled n and $(n-1)$ represent the levels of the "hydrogenic manifold" of states, that is, states for which the quantum defect is so small that the difference in energy between them cannot be seen on this scale; for sodium the hydrogenic manifolds comprise states for which $l \geqslant 2$. The locations of the s and p states, which have quantum defects of 1.35 and 0.85, respectively, are always located as shown with respect to the difference between hydrogenic manifolds, $1/n^3$ in atomic units.

As the field is turned on, the energy of the p-state increases quadratically. Quantum mechanically this is expected because the p-state is "repelled" by the nearest state, in the case of sodium the highest of the hydrogenic states of the lower manifold of the proper symmetry. The increase in energy of the p state is, however, difficult to reconcile by envisioning polarization of a charge distribution. Such an increase corresponds to a negative polarizability!

The situation can be clarified by considering the effect of the field on the precessing elliptical orbit as shown Fig. 3(a). As is apparent by counting apsides on each side of a line through the force center and perpendicular to F, the precession rate is slower on the "downfield" side causing a

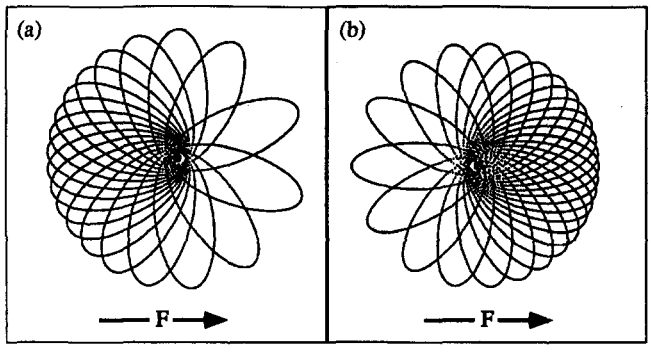

Fig. 3. Precession of a nearly Keplerian elliptical orbit of the Rydberg electron about a positively charged nucleus in an electric field $F = 1000$ V/cm. The precession is produced by adding a term $-\alpha_d/2r^4$ to the Coulomb potential. The principal quantum number n is 10. The orbital angular momentum quantum number l would be 5 in the absence of **F**, but due to the presence of the field angular momentum is not conserved. The magnetic quantum number m_l was chosen to be zero for convenience; this choice makes the angular momentum vector perpendicular to F. (a) $\alpha_d = +40$ a.u. (b) $\alpha_d = -40$ a.u.

buildup of negative charge on that side, as expected. Recall that it is the negatively charged electron that is executing the near Keplerian motion about the positively charged nucleus. As discussed above, such a situation results in a negative energy shift and corresponds to the case in which the isolated (zero-field) state is closer to the hydrogenic manifold above than below.

If, however, the state is closer to the manifold below, as is the case for p-states of sodium, then the rate of change of the quantum defect with angular momentum is positive rather than negative, causing the orbit to precess in the opposite direction [see Eq. (23)]. Note that we may ignore the integer part of δ_l, the only effect of which is on the ordering of the states with respect to n. The positive rate of change resulting from the proximity to the lower manifold causes the Keplerian orbit to precess in the "wrong direction," leading to a negative charge buildup "upfield," and thus a negative polarizability. This is shown in Fig. 3(b), where, although the field **F** is in the same direction as that for Fig. 3(a), the charge distribution is polarized opposite to the direction of the field. We must of course restrict our conception of angular advance or retreat of the apside to values between 0 and π per Keplerian orbit.

The above discussion ignores the cause of any negative polarizability. All that is required is that the isolated level be closer to the lower manifold than the upper. In fact, in sodium, for which $\delta_0 = 1.35$, the s states are displaced further than the p states, but, because the fractional part of the quantum defect is less than one-half, s states are closer to the hydrogenic manifold above and their quadratic Stark shifts are down. Nonetheless, from a classical point of view, it is much more revealing to consider the direction and rates of precession of the Keplerian orbit than the effect of a field on a distribution of charge.

At higher values of electric field the precession rate about **F** will overtake the core precession; again both are assumed small compared to the electronic orbital frequency. In this case the atom will behave in a hydrogenic fashion for individual electronic orbits, each of which will precess about **F** without substantial change in shape. It is therefore expected that, at sufficiently high electric fields, Rydberg atoms will exhibit a linear Stark effect. Indeed, this is observed,[1] but, because the electric dipole moment of an electron in Keplerian orbit about a proton is proportional to n^2 (see I), these "high" electric fields are not high at all by ordinary laboratory standards. Thus the quadratic Stark effect on the states that constitute the hydrogenic manifold of a Rydberg atom is usually not evident on a map such as the one depicted in Fig. 2. This might lead to the assumption that those zero field states for which $l > (n/2)$ have negative polarizability since their energies increase as the electric field increases. This is not the case, however, because the increase results from the *linear* Stark effect on states for which the permanent electric dipole moments are aligned in opposition to the electric field. Indeed, if the region near $F = 0$ of a Stark map for a Rydberg atom were magnified to a degree that makes the nondegenerate nature of the zero-field states evident, thus permitting observation of the quadratic Stark effect, it would be seen that as F increases, these energies first decrease quadratically, but subsequently increase linearly. This is clearly illustrated in Fig. 1 of Ref. 4 that shows the low field region for the $n = 10$ hydrogenic manifold of sodium. In terms of the discussion in this paper, the initial decrease is a result of the regular nature of the quantum defects for high l states, that is, the fractional part of these quantum defects are all less than one-half and, moreover, they decrease with increasing l. From a quantum mechanical viewpoint, the initial decrease in energy of a given state results from repulsion by the level above inasmuch as the state in question is closer to the above level than the one below it.

In early experiments the difficulty associated with maintaining high electric fields without breakdown made Stark effect experiments difficult to perform. With the availability of lasers, however, it has become possible to produce substantial concentrations of atoms in specific high-lying states; accordingly, the study of the Stark effect in atoms has undergone a rebirth.[1,12–14] In fact, precision Stark spectroscopy on very high-lying states, in conjunction with quantum defect theory, has recently been employed to determine atomic energies, including ionization potentials, to new levels of accuracy.[14]

The approximate value of the field at which the linear Stark effect manifests itself in Rydberg atoms can be estimated by noting that the quantum mechanical analog of the condition for "high" fields is that the Stark energy shifts are larger than energy differences between adjacent angular momentum states of the same n manifold. This has already been calculated [Eq. (22)]. We therefore set ω_{rad} equal to the Stark energy

$$E_{\text{Stark}} = \mathbf{d}\cdot\mathbf{F} \simeq (\tfrac{3}{2})n^2|\mathbf{F}|\epsilon. \tag{25}$$

Solving for $|\mathbf{F}|$ we obtain

$$|\mathbf{F}| = (\tfrac{5}{2})\alpha_d(1/n^5 l^6)(1/\epsilon). \tag{26}$$

Again, the result is identical to that of Freeman and Kleppner[4] using their quantum mechanical treatment.

In addition to the results derived above, it is possible to extract many other atomic properties using this classical picture. For example, the atomic polarizability may be derived by averaging the Keplerian dipole moment[2] over a precessional period. In many cases the results are identical with those of a quantum mechanical perturbation treatment. Thus using visualization provided by a classical picture, together with the insight required for proper applica-

tion of the correspondence principle, the mechanics of multielectron atoms may be better understood.

APPENDIX: THE GRAVITATIONAL DEFECT OF MERCURY

It has long been known that the perihelion of the Keplerian orbit of the planet Mercury advances by 574″ of arc per century.[6] Of this 574″, approximately 531″ can be accounted for by Newtonian perturbations of Mercury's orbit by other planets. The remaining 43″ has been shown to result from relativistic corrections to the Newtonian force law that can be represented by an additional attractive term, proportional to $1/r^3$, in the potential energy.[15] Since this term is small compared to the $1/r$ term, we may consider the motion of the orbit resulting from the $1/r^3$ perturbations. This perturbation also leads to a small deviation from the Keplerian energy, a deviation that may be described in terms of a "gravitational defect" by analogy with the quantum defect. Since we have established that the defect and the precession are only different manifestations of the same perturbation, the formalism that was used in the atomic case may be employed. The dependence of the gravitational defect on angular momentum will differ from that of the quantum defect because the perturbation has a different r dependence, but the magnitude of the gravitational defect may be computed.

To investigate the magnitude of the gravitational defect γ we abandon atomic units and write the potential energy as

$$V(r) = -K/r - H/r^3, \tag{A1}$$

where $K = GmM$ with m the mass of Mercury and M the mass of the Sun; G is the gravitational constant. Now, Mercury occupies one of an infinity of allowed Keplerian orbits, the energies of which are given by

$$E_K = -K/2a, \tag{A2}$$

where a is the semimajor axis of the elliptical orbit. Although it is not necessary to do so, we maintain the analogy with atomic systems by quantizing this gravitational system as is occasionally done as an exercise in introductory quantum mechanics. The quantization is easily effected by replacing a with $n^2 a_{go}$ (since we already know the answer for a $1/r$ potential) where a_{go} is the analog of the Bohr radius and is given by

$$a_{go} = \hbar^2/mK, \tag{A3}$$

where, as above, m is the mass of Mercury and $\hbar$ is Planck's constant divided by 2π. In reality, m should be replaced by the Mercury–Sun reduced mass. Of course a_{go} is a tiny number, as it must be when the laws of quantum mechanics are applied to a macroscopic system. Nevertheless, we will temporarily retain it.

To account for the correction to the Keplerian energy resulting from the $1/r^3$ term in the potential energy, we introduce the gravitational defect γ. The true energy E is thus given by

$$\begin{aligned} E &= -K/2a_{go}(n-\gamma)^2 \\ &= E_{Ko}/n^2(1-\gamma/n)^2, \end{aligned} \tag{A4}$$

where E_{Ko} is the "ground state" energy of Mercury which, because Mercury is bound, is negative. If $\gamma \ll n$ we may write

$$E = E_{Ko}/n^2 + (2E_{Ko}/n^3)\gamma, \tag{A5}$$

which is analogous to Eq. (4).

Now the second term in Eq. (A5) clearly represents the correction to the Keplerian energy and may be equated to the value of the $1/r^3$ perturbing term $\langle \Delta E \rangle$, averaged over a Keplerian period τ. We have

$$\langle \Delta E \rangle = \frac{1}{\tau}\int_0^\tau \left(-\frac{H}{r^3}\right) dt. \tag{A6}$$

Using Keplers second law and the equation of the Keplerian orbit, this integral, which is easily evaluated, is

$$\langle \Delta E \rangle = -2\pi m^2 HK/l^3\tau, \tag{A7}$$

from which it follows that

$$\gamma = \sqrt{K/a_{go}m}\ [m^2 H/l^3]. \tag{A8}$$

Now, we are really interested in the value of $(1-\gamma/n)$, the correction factor to the Keplerian energy. We may therefore rescale, for convenience, the principal quantum number with $n = 1$ now corresponding to the energy of Mercury in the orbit that it occupies. This rescaling merely requires replacing a_{go} by $a_M \cong 58\times 10^9$ m, the semimajor axis of Mercury's orbit. Letting $l = mv_M a_M$, where v_M is the orbital velocity of Mercury, we find $\gamma = 2.5\times 10^{-8}$. As expected, a defect for such a nearly circular orbit is very small, but, judging from the 19th century observations of the advance of Mercury's perihelion, clearly not negligible.

Finally, we may formulate, by analogy with the correspondence principle derivation leading to Eq. (23), an expression for the precessional frequency of Mercury's orbit, ω_p. Equating the energy difference between adjacent l states for a given n to $\hbar\omega_p$, we have

$$\begin{aligned} \hbar\omega_p &= \frac{2E_{Ko}}{n^3}\left[\gamma_{l+1} - \gamma_l\right] \\ &= \frac{2E_{Ko}}{n^3}\frac{\partial\gamma}{\partial l}\Delta l. \end{aligned} \tag{A9}$$

Since $\Delta l \equiv \hbar$, we arrive at

$$\begin{aligned} \omega_p &= -\frac{2\pi}{\tau}\frac{\partial\gamma}{\partial l}\sqrt{ma_M K} \\ &= \frac{6\pi m^2 HK}{\tau l^4}, \end{aligned} \tag{A10}$$

where Kepler's third law was used to convert a_M into τ. This result is identical to that derived using classical perturbation theory.[8] Evaluation of this expression with $l = mv_M a_M$ shows that, as expected, $\omega_p = 43''$/ century.

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Floating equilibrium of symmetrical objects and the breaking of symmetry. Part 1: Prisms

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The equilibrium configurations of solid prisms of square and equilateral triangular cross section floating in a liquid are examined. It is found that these bodies float in different symmetrical or asymmetrical positions with respect to the vertical plane depending on the solid–liquid specific mass ratio, or depending on the height at which the body's axis is held above the liquid level.

I. INTRODUCTION AND HISTORY

During a lunch-table conversation, Professor Brian Pippard told one of us about his experience with students who were given the following problem: A solid and homogeneous prism of square cross section and great length compared to its diagonal is floated on a liquid. The longitudinal axis of the prism is not allowed to deviate from the horizontal position, but the prism may turn freely around this axis.

The question that was asked the students was the following: Given the specific mass of the liquid and the specific mass of the solid, in which position will the prism float? As Professor Pippard indicated, this problem, although elementary, taxed many students beyond their capacity.

In fact, this problem has a distinguished history.

The subject of the flotation of homogeneous solid bodies in liquids has been treated by Chr. Huygens in 1650 (see Fig. 1):[1] He was 21 years old at the time. He revised the paper "De iis quae liquido supernatant" several times later in his life. His only quoted reference on this subject is Archimedes.[2] It seems that Huygens was the first person who treated the flotation of a long prism of rectangular cross section and he discovered that in certain ranges of the ratio of the specific masses of the solid and liquid, this symmetrical object will float in an asymmetrical stable equilibrium position. This discovery was not entirely new, since Archimedes already noted that a truncated paraboloid of revolution (a symmetrical body) may float in an equilibrium position unrelated to its symmetry.[2,3]

It is not known why Archimedes chose to study the flotation of a truncated paraboloid of revolution. A reason may have been that, previously, he had proved many propositions concerning the geometry of parabolas. Also, he may have observed watermelon halves floating in the bay of Syracuse, Sicily, where he lived. The mathematical formalism of his time did not allow him to express the angle of flotation in a formula (e.g., no trigonometric functions were known); instead, he described how to construct a triangle geometrically with one angle identical to the angle of flotation, given the ratio of the densities of the solid and of the liquid.

Huygens did not arrive at a complete solution of the problem of long prisms, insofar as he probably did not recognize the existence of a stable equilibrium position in which either one or three edges of the prism are below the liquid surface, although he treated the case where two edges are submerged. The former positions are only stable