

## Evaluation of some averages for the hydrogen atom

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then a transparency is made from it, it may be desirable to incorporate a small correction factor into the equations for  $X$  and  $Y$ , since many copiers do not produce copies of identical size as the original.

Now that overlays can be easily obtained, the student can set up the apparatus at any convenient spacing, and then produce the corresponding Greninger net. The method of using the net for analysis of a film is described by Nuffield and in greater detail by Cullity.<sup>4</sup>

It is a straightforward matter to incorporate the above equations into a computer program to generate the Greninger plot, but if anyone is interested in obtaining a Fortran

version of such a program, which directs its output to a Complot plotter, I will be glad to send them a listing of the program used to generate Fig. 1.

<sup>1</sup>K. Ravindhran *et al.*, *J. Appl. Phys.* **50**, 5030 (1979) discusses an algorithm for solving cubic crystal backreflection Laue patterns.

<sup>2</sup>A. Greninger, *Z. Kristallog.* **91**, 424 (1935).

<sup>3</sup>E. Nuffield, *X-Ray Diffraction Methods* (Wiley, New York, 1966), pp. 230–235.

<sup>4</sup>B. D. Cullity, *Elements of X-Ray Diffraction*, 2nd ed. (Addison-Wesley, Reading, MA, 1978), pp. 233–247.

## Evaluation of some averages for the hydrogen atom

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The calculation of the average value of any power of the radius for the hydrogen atom is rather tedious and requires good knowledge of the associated Laguerre polynomials.<sup>1</sup> That is why in most books on atomic physics only the results are presented.<sup>2,3</sup> Among all the averages, three ( $\langle r^{-1} \rangle$ ,  $\langle r^{-2} \rangle$ , and  $\langle r^{-3} \rangle$ ) are very important because they are necessary to calculate the relativistic corrections leading to the fine structure of the hydrogen levels. It is the purpose of this note to show how to evaluate these average values in a very simple way.

Let us remember that the Hamiltonian for the radial part of the hydrogenlike wave functions is (in Hartree units and obvious notation)

$$H = -\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{l(l+1)}{2r^2}. \quad (1)$$

The corresponding Schrödinger equation  $HP_{nl}(r) = E_n P_{nl}(r)$  with the boundary conditions  $P_{nl}(0) = P_{nl}(\infty) = 0$  yields the eigenvalues

$$E_n = -Z^2/2n^2, \quad (2)$$

which are the energy levels in the nonrelativistic theory of hydrogenlike atoms.

For the calculation of  $\langle r^{-1} \rangle$  and  $\langle r^{-2} \rangle$  we shall use the Hellmann–Feynman theorem<sup>4</sup>

$$\frac{\partial E_i}{\partial \lambda} = \left\langle \phi_i \left| \frac{\partial H}{\partial \lambda} \right| \phi_i \right\rangle. \quad (3)$$

Here  $\lambda$  is any parameter in the Hamiltonian  $H$ ;  $\phi_i$  and  $E_i$  are an eigenfunction and its corresponding eigenvalue of  $H$ , respectively. A proof of the theorem is very simple. According to first-order perturbation theory a change  $\Delta H$  in the Hamiltonian produces a change  $\Delta E_i$  in the eigenvalue given by

$$\Delta E_i = \langle \phi_i | \Delta H | \phi_i \rangle.$$

This equation is only approximate if  $\Delta H$  and  $\Delta E$  are finite. But if the changes are infinitesimal the result is exact and the Hellmann–Feynman theorem follows.

If we take  $Z$  from (1) and (2) as the parameter in (3) we obtain in the right-hand side of (3) the expectation value of  $(-1/r)$ . Hence,

$$\langle 1/r \rangle = Z/n^2. \quad (4)$$

This way of evaluating  $\langle r^{-1} \rangle$ , which can also be obtained by means of the virial theorem, is well known.

Less obvious is the fact that we can use expression (3) to get  $\langle r^{-2} \rangle$ . It is necessary to remember that the principal quantum number  $n$  is equal to  $l + k$ ,  $k$  being the number of nodes of the radial wave function  $P_{nl}(r)$  (excluding the node for  $r = 0$  but including the one for  $r = \infty$ ). This fact enables the calculation of both derivatives in (3) if we take the parameter  $\lambda$  to be  $l$  (i.e., the angular momentum quantum number). The result is

$$\langle 1/r^2 \rangle = Z^2/n^3(l + 1/2). \quad (5)$$

In order to get  $\langle r^{-3} \rangle$  one has to proceed differently. Let us apply the operator  $d/dr$  to both sides of the Schrödinger equation  $HP_{nl}(r) = EP_{nl}(r)$ , multiply on the left by  $P_{nl}(r)$ —since this function is real—and integrate over  $r > 0$ . We obtain

$$\begin{aligned} \langle P_{nl} | H | P'_{nl} \rangle + \left\langle P_{nl} \left| \frac{Z}{r^2} - \frac{l(l+1)}{r^3} \right| P_{nl} \right\rangle \\ = E_n \langle P_{nl} | P'_{nl} \rangle, \end{aligned} \quad (6)$$

where  $P'_{nl}$  means the derivative of  $P_{nl}$  (we have omitted the variable  $r$  in these functions). Since

$$\langle P_{nl} | H | P'_{nl} \rangle = \langle P'_{nl} | H | P_{nl} \rangle$$

(except for  $l = 0$  because the functions  $P'_{n0}$  are not zero at the origin) and  $P_{nl}$  are eigenfunctions of the Schrödinger equation, the first term of the left-hand side of (6) cancels the right-hand side and we get

$$\left\langle P_{nl} \left| \frac{Z}{r^2} - \frac{l(l+1)}{r^3} \right| P_{nl} \right\rangle = 0, \quad (7)$$

which, as mentioned before, is not valid for  $l = 0$ . Equation (7) relates  $\langle r^{-3} \rangle$  to  $\langle r^{-2} \rangle$ . Having already the result (5), we obtain immediately

$$\frac{1}{r^3} = \frac{Z^3}{n^3(l+1)(l+1/2)l}. \quad (8)$$

Formulas (4), (5), and (8) are the results we were looking for. We can notice that the physical meaning of (7) is that

the force on the electron due to the Coulomb attraction of the nucleus equals the centrifugal force; the former remark that (7) is not valid for  $l = 0$  expresses the fact that the corresponding quantum states do not have a classical analog. Those readers who are ready to accept without proof that (7) is the quantum equivalent of the above mentioned classical equilibrium of Coulomb and centrifugal forces will reach the result (8) at once.

<sup>1</sup>H. A. Bethe and E. E. Salpeter, *Handbuch der Physik* (Springer, Berlin, 1957), Vol. 35, p. 99.

<sup>2</sup>E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, 1951), p. 117.

<sup>3</sup>I. I. Sobel'man, *Introduction to the Theory of Atomic Spectra* (Pergamon, Oxford, 1972), p. 9.

<sup>4</sup>M. Weissbluth, *Atoms and Molecules* (Academic, New York, 1978), p. 555.

## Simple *F*-center argument from the uncertainty principle

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*F* centers<sup>1</sup> are "color centers" of the type where an electron is trapped in a lattice vacancy. This note presents a naive uncertainty principle argument for a certain regularity in the *F*-center data.

Assuming the electron trapped in a cubical box of side  $2a$ , leads to the usual  $x$ ,  $y$ , and  $z$  momentum uncertainties of at least

$$\hbar/2a.$$

Since the average  $x$  component of momentum is zero, and likewise for  $y$  and  $z$  components, the kinetic energy uncertainty comes out to at least

$$3\hbar^2/8ma^2.$$

If we interpret the minimum kinetic energy uncertainty as the difference between the ground-state energy and the energy of the first excited state, then a ground-state electron would pick up this much energy when absorbing a photon, and jumping to the first excited state.

Thus the kinetic energy uncertainty, which is proportional to the inverse square of the box length in which it is trapped, is also proportional to the inverse of the wavelength strongly absorbed in the *F* center, so

$$\lambda/a^2$$

Table I. *F*-center data.

Alkali halide	Spacing $a(\text{\AA})$	<i>F</i> -center wavelength ( $\text{\AA}$ )	$\lambda/a^2 (\text{\AA}^{-1})$
LiF	2.01	2500	619
NaF	2.31	3410	639
LiCl	2.57	3850	583
KF	2.67	4550	638
NaCl	2.81	4580	580
NaBr	2.98	5400	608
KCl	3.14	5560	564
NaI	3.23	5880	564
RbCl	3.27	6090	570
KBr	3.29	6250	577
RbBr	3.43	6940	590
KI	3.53	6890	553
RbI	3.66	7560	564

should be a constant over all the various *F* centers.

Table I gives a brief summary of calculations based on data from Ref. 1. The reader may judge from this whether  $\lambda/a^2$  is sufficiently "constant."

<sup>1</sup>G. P. Hughes, *Am J. Phys.* **45**, 948. (1977).

## Bohr orbit model and Ruedenberg's theory of the origin of the binding energy for $H_2$

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### I. INTRODUCTION

Ruedenberg has demonstrated<sup>1</sup> that the origin of the binding energy for the hydrogen molecule arises from a "crucial depression" in kinetic energy that occurs when electron charge accumulates in the internuclear (bond) region. With orbital theory, the transfer of charge from near

the nuclei into the bond region on molecule formation is a consequence of the constructive interference of the atomic orbitals when they overlap. More recent publications by Ruedenberg and his co-workers<sup>2</sup> and others<sup>3</sup> lend further support to Ruedenberg's deduction concerning the role of kinetic energy in bonding for both  $H_2^+$  and  $H_2$ .

In each of Refs. 1-3, the wavelike character of the elec-