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Relativistic Quantum Chemistry

The electrons and the nodes

Many students in their first exposure to quantum mechanics are puzzled by the nodes in the position probability density, i.e., of surfaces in space at which the probability an electron be there is exactly zero. They ask, "How do the electrons get across the nodes?"

A particularly satisfying answer has been at hand since 1928, when Paul A. M. Dirac published a two-part paper (1) which has recently been described (2, p. 187) as "undoubtedly one of the great papers in physics of this century." Namely, there aren't any nodes. When an electron problem is solved by Dirac's relativistic treatment, as it properly must be, the solution differs in a number of major respects from that of Schrödinger's nonrelativistic treatment. One of the minor, but interesting, consequences is that the nodal surfaces which resulted from the Schrödinger approximation are replaced by regions in which the position probability density, although small, is always finite.

This simple result has a surprisingly scanty publication history. In 1931, Harvey White published (3), as a sequel to his famous electron-cloud pictures of a Schrödinger atom, the electron-cloud pictures of the corresponding Dirac atom. He there commented on the nonexistence of radial nodes in the Dirac electron cloud, and, too, on the nonexistence of angular nodes, although, as we shall see later, the reason for the nonexistence of angular nodes is somewhat different. A great many textbook authors, including myself, have copied White's Schrödinger pictures instead of his more correct Dirac pictures, and we all seem to have ignored his observations about the nodes. In a 1965 paper (4) devoted to the computation of relativistic self-consistent-field eigenfunctions for all the atoms of the periodic table, Waber and Cromer made passing comment on, and gave the correct explanation for, the nonexistence of radial nodes. Seel, in his little book "Atomic Structure and Chemical Bonding," (5, p. 14), raised the question of how the electrons pass through the nodes, and said that the answer was to be found in Dirac's treatment of the atom. However, he did not carry the explanation far enough for a reader to see why this is so, and with the comment, "Unfortunately, the elegance of this more general theory is bought at the expense of considerably more mathematical effort," he dropped the subject.

In fact, Dirac's mathematical techniques do not nowadays look so difficult as all that. We hardly feel constrained to say, as Darwin said in 1928 (6),

There are probably readers who will share the present writer's feeling that the methods of non-commutative algebra are harder to follow, and certainly much more difficult to invent, than are operations of types long familiar to analysis. Wherever it is possible to do so, it is surely better to present the theory in a mathematical form that dates from the time of Laplace and Legendre...

A good many of today's students are familiar with the matrix methods which Dirac used. Consequently, there may be some usefulness in collecting here in one place the key results of Dirac's treatment, now mostly to be found scattered through the literature, and to work out explicitly some results likely to be of interest to chemists.

Outline of the Dirac Treatment

This is not the place to go into the philosophy underlying Dirac's procedure. A most readable exposition of it is to be found in Sherwin's textbook (7). In brief, Dirac's starting point to find the energy E of an electron subject to a scalar potential V, with rest mass m and momenta p_x, p_y, and p_t, was the Hamiltonian equation in the form

$$E = -\alpha_x p_x c - \alpha_y p_y c - \alpha_z p_z c - \beta m c^2$$

This form was chosen because, when squared, it leads to the relativistically correct equation

$$E^2 = p_x{}^2 c^2 + p_y{}^2 c^2 + p_z{}^2 c^2 + m^2 c^4$$

provided the operators α_x, α_y, α_z, and β each give unity when squared, and the product of any two of them merely changes sign when their order of multiplication is reversed—they anticommute. The α's are usually called the Dirac velocity operators, and β the Dirac aspect operator. To convert the classical Hamiltonian into a quantum-mechanical Hamiltonian one proceeds as usual, construing E as a scalar operator and p_x as the differential operator $-i\hbar\, \partial/\partial x$, operating on an eigenfunction ψ. The effect of a scalar potential V is found to be taken into account properly if E is replaced by $(E - V)$, giving finally

$$(E - V)\psi = i\hbar c \left(\alpha_x \frac{\partial}{\partial x} + \alpha_y \frac{\partial}{\partial y} + \alpha_z \frac{\partial}{\partial z} \right) \psi - \beta m c^2 \psi$$

The reader will surely notice that this is not identical with Schrödinger's equation.

Dirac then went on to show (for an elegant modern demonstration of the same point cf. (2), p. 194) that the conditions imposed on the α's and β could not be satisfied if they and ψ were scalar functions; nor if they were 2×2 matrices and ψ the corresponding 2-component vector; nor if they were 3×3 matrices and ψ a 3-component vector; they had to be at least 4×4 matrices and ψ a 4-component vector. When ψ is written as a 4-component column vector,

$$\psi = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}$$

the position probability density is obtained by premultiplying it by its complex conjugate row vector, thus

$$\psi^*\psi = [\psi_1{}^*, \psi_2{}^*, \psi_3{}^*, \psi_4{}^*] \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}$$

where the asterisk indicates that the imaginary unit i must be replaced by $-i$. Following the usual rules for multiplying a row-vector by a column-vector (to wit, first component times first, second times second, etc.), one obtains for the position probability density

$$\psi^*\psi = \psi_1{}^*\psi_1 + \psi_2{}^*\psi_2 + \psi_3{}^*\psi_3 + \psi_4{}^*\psi_4$$

Inasmuch as each of the four terms is non-negative, the position probability density can never be negative—a physically gratifying result. The Dirac velocity operators and aspect operator are usually written out as follows

$$\alpha_x = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$$

$$\alpha_y = \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix}$$

$$\alpha_z = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix}$$

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

The reader may satisfy himself that these operators do give unity when squared and that any pair of them anticommute.

This matrix notation for the Dirac Hamiltonian is really a shorthand way of saying that not one but four differential equations have to be satisfied, and, when one actually has to carry out the solution, he multiplies out the vectors by the matrices in full and solves the four simultaneous equations that result.

The explicit solution of the Dirac Hamiltonian for a hydrogenlike atom, viz., an atom with a central scalar potential $V = -Ze/r$, was first published by Darwin in 1928 (2). An excellent modern presentation of it is in Bethe and Salpeter's monograph (8). The procedure is much like that used to solve the corresponding Schrödinger problem. One first expresses the eigenfunction as a product of a radial factor and an angular factor, and finds that this leads to the separation of the Hamiltonian into an angular equation and a radial equation. The angular equation can be solved in terms of spherical harmonics and certain angular quantum numbers, the radial equation solved in the form e^{-cr} multiplied by a terminating power series in r, with certain radial quantum numbers. Four quantum numbers are required to specify the state of a Dirac hydrogenlike atom, but these are not exactly the same as the four familiar quantum numbers of the Schrödinger atom, because orbital angular momentum and spin angular momentum, taken separately, are not constants of motion and therefore cannot be represented by good quantum numbers. The Dirac quantum numbers are:

First, n, the principal quantum number, which can take values 1, 2, 3, 4 ... and has much the same physical meaning as for the Schrödinger atom.

Second, l, the azimuthal quantum number, which (as for the Schrödinger atom) can take values 0, 1, 2 ... $(n - 1)$, and is usually denoted by letters s, p, d, f, etc. The difference is that l no longer represents an orbital angular momentum.

Third, j, the angular momentum quantum number, sometimes called the inner quantum number. It is always positive and can take at most two values, $|l \pm 1/2|$. It is usually denoted by a subscript following the azimuthal quantum number.

Fourth, m, the magnetic quantum number, which can take all half-odd-integer values from $-j$ to $+j$.

The energy level diagram for a Dirac hydrogenlike atom (Fig. 1) differs slightly from that for the Schröd-
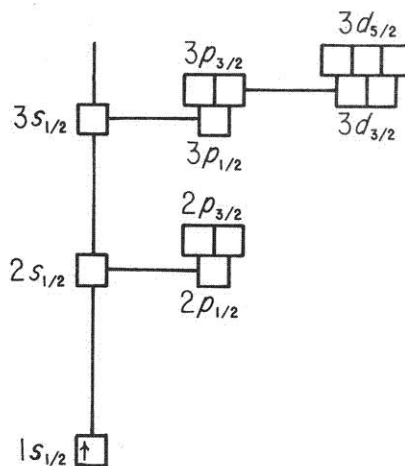

Figure 1. Dirac pigeonhole diagram for a hydrogenlike atom. Not drawn to scale: in particular, the energy separation between fine-structure subgroups is greatly exaggereated in this diagram. Each energy level is more negative than in the Schrödinger treatment by a fraction of its value equal to $(Z/137)^2$ multiplied by the following: for $1s_{1/2}$, $1/4$; for $2p_{3/2}$, $1/64$; for $2s_{1/2}$ and $2p_{1/2}$, $5/64$; for $3d_{5/2}$, $1/324$; for $3p_{3/2}$ and $3d_{3/2}$, $3/324$; for $3s_{1/2}$ and $3p_{1/2}$, $11/324$. The general expression for the fractional lowering is

$$(Z/137)^2 \left(\frac{n}{j + 1/2} - 3/4 \right) \Big/ n^4$$

inger atom, in that the three p levels, the five d levels, etc., are no longer degenerate. There is a small splitting in energy between those levels of higher and those of lower j value. This "fine-structure" splitting had long been known experimentally, and it was a great triumph of Dirac's treatment to predict this splitting and even to give its correct numerical value. The phenomenon is sometimes, even today, ascribed to "spin-orbit" interaction, perhaps an unfortunate name inasmuch as spin angular momentum and orbital angular momentum are not, separately, defined in Dirac's theory. Moreover (and this had been known earlier) the shift of energy is greatest for s states, which were not supposed to have any orbital angular momentum. Fortunately, there is a way to resolve this seeming discrepancy (cf. section on the *Zitterbewegung* Approach).

A display of the Dirac eigenfunctions for the $1s$, $2s$, and $2p$ states is presented in Table 1. A reader who wishes to try his mettle by computing, say, the $3d$ functions, is encouraged to turn to the Appendix where he will find the general expression.

The four components of a Dirac eigenfunction are familiarly named, reading from top to bottom, as follows: large spin-up component, large spin-down component, small spin-down component, small spin-up com-

Table 1. Dirac Eigenfunctions. (Radial Distance r in Units of a/Z. Eigenfunctions in units of $(Z^3/\pi a^3)^{1/2}$. Radial functions to order αZ only.)

$1s_{1/2},\ m = +^1/_2$

$$\begin{bmatrix} e^{-r} \\ 0 \\ ^1/_2 i\alpha Z e^{-r}\cos\theta \\ ^1/_2 i\alpha Z e^{-r}\sin\theta e^{i\phi} \end{bmatrix}$$

$1s_{1/2},\ m = -^1/_2$

$$\begin{bmatrix} 0 \\ -e^{-r} \\ -^1/_2 i\alpha Z e^{-r}\sin\theta e^{-i\phi} \\ ^1/_2 i\alpha Z e^{-r}\cos\theta \end{bmatrix}$$

$2s_{1/2},\ m = +^1/_2$

$$\sqrt{^1/_8}\begin{bmatrix} e^{-r/2}\left(1 - \dfrac{r}{2}\right) \\[4pt] 0 \\[4pt] ^1/_2 i\alpha Z e^{-r/2}\left(1 - \dfrac{r}{4}\right)\cos\theta \\[4pt] ^1/_2 i\alpha Z e^{-r/2}\left(1 - \dfrac{r}{4}\right)\sin\theta e^{i\phi} \end{bmatrix}$$

$2s_{1/2},\ m = -^1/_2$

$$\sqrt{^1/_8}\begin{bmatrix} 0 \\[4pt] -e^{-r/2}\left(1 - \dfrac{r}{2}\right) \\[4pt] -^1/_2 i\alpha Z e^{-r/2}\left(1 - \dfrac{r}{4}\right)\sin\theta e^{-i\phi} \\[4pt] ^1/_2 i\alpha Z e^{-r/2}\left(1 - \dfrac{r}{4}\right)\cos\theta \end{bmatrix}$$

$2p_{1/2},\ m = +^1/_2$

$$\sqrt{^1/_{32}}\begin{bmatrix} -\sqrt{^1/_3}\,re^{-r/2}\cos\theta \\[4pt] -\sqrt{^1/_3}\,re^{-r/2}\sin\theta e^{i\phi} \\[4pt] \sqrt{^3/_4}\,i\alpha Z e^{-r/2}\left(1 - \dfrac{r}{6}\right) \\[4pt] 0 \end{bmatrix}$$

$2p_{1/2},\ m = -^1/_2$

$$\sqrt{^1/_{32}}\begin{bmatrix} \sqrt{^1/_3}\,re^{-r/2}\sin\theta e^{-i\phi} \\[4pt] -\sqrt{^1/_3}\,re^{-r/2}\cos\theta \\[4pt] 0 \\[4pt] \sqrt{^3/_4}\,i\alpha Z e^{-r/2}\left(1 - \dfrac{r}{6}\right) \end{bmatrix}$$

$2p_{3/2},\ m = +^3/_2$

$$\sqrt{^1/_{32}}\begin{bmatrix} \sqrt{^1/_2}\,re^{-r/2}\sin\theta e^{i\phi} \\[4pt] 0 \\[4pt] \sqrt{^1/_{32}}\,i\alpha Z r e^{-r/2}\sin\theta\cos\theta e^{i\phi} \\[4pt] \sqrt{^1/_{32}}\,i\alpha Z r e^{-r/2}\sin^2\theta e^{2i\phi} \end{bmatrix}$$

$2p_{3/2},\ m = -^3/_2$

$$\sqrt{^1/_{32}}\begin{bmatrix} 0 \\[4pt] \sqrt{^1/_2}\,re^{-r/2}\sin\theta e^{-i\phi} \\[4pt] \sqrt{^1/_{32}}\,i\alpha Z r e^{-r/2}\sin^2\theta e^{-2i\phi} \\[4pt] -\sqrt{^1/_{32}}\,i\alpha r Z e^{-r/2}\sin\theta\cos\theta e^{-i\phi} \end{bmatrix}$$

$2p_{3/2},\ m = +^1/_2$

$$\sqrt{^1/_{32}}\begin{bmatrix} \sqrt{^2/_3}\,re^{-r/2}\cos\theta \\[4pt] -\sqrt{^1/_6}\,re^{-r/2}\sin\theta e^{i\phi} \\[4pt] \sqrt{^3/_{32}}\,i\alpha Z r e^{-r/2}(\cos^2\theta - ^1/_3) \\[4pt] \sqrt{^3/_{32}}\,i\alpha Z r e^{-r/2}\sin\theta\cos\theta e^{i\phi} \end{bmatrix}$$

$2p_{3/2},\ m = -^1/_2$

$$\sqrt{^1/_{32}}\begin{bmatrix} -\sqrt{^1/_6}\,re^{-r/2}\sin\theta e^{-i\phi} \\[4pt] -\sqrt{^2/_3}\,re^{-r/2}\cos\theta \\[4pt] -\sqrt{^3/_{32}}\,i\alpha Z r e^{-r/2}\sin\theta\cos\theta e^{-i\phi} \\[4pt] \sqrt{^3/_{32}}\,i\alpha Z r e^{-r/2}(\cos^2\theta - ^1/_3) \end{bmatrix}$$

ponent. The two components called "small" are smaller than those called "large" by a factor of the order (speed of the electron)/(speed of light), namely $Z/137$, usually written αZ.

The Radial Nodes

The same large radial factor, called g, applies to both the large components, and the same small radial factor, f, to both the small components.

The only instances in which f is merely a multiple of g are those in which both are nodeless anyway, namely the $1s_{1/2}$, $2p_{3/2}$, $3d_{5/2}$, etc., states. For these states the power series in r terminates with its first term, so that both g and f are proportional to $r^{n-1}e^{-r/n}$. The proof of this result is assigned as a homework problem by Messiah in his textbook ((9), v. **2**, p. 958) with the hint that it can be done by a systematic search; in fact, it can be seen by inspection of the general expression for the radial factors (Appendix).

When g has two or more terms in its power series, so has f. But the coefficients in the power series are always different, so that the nodes in g never fall in the same place as the nodes in f. Consider, for example, the $2s_{1/2}$ orbital, which on the Schrödinger treatment has a radial node at $r = 2$. In the Dirac treatment the large component has a radial node at $r = 2$, but the small component has its radial node at $r = 4$. Consequently, the position probability density at $r = 2$ has a finite contribution from the small component (Fig. 2).

This result is general. In summary, at the Schrödinger radial "nodes" the relativistic treatment leads to

a residual probability density of the order of $(Z/137)^2$ $r^{2n-2}e^{-2r/n}$.

The Angular Nodes

The question of angular nodes must be examined in a little more detail, because we must distinguish between the angular dependence of position probability density for an isolated atom ("spectroscopists' atom") and that for an atom within a molecule ("chemists' atom").

Consider first the isolated atom, perhaps in a weak field. The problem can be simplified by Hartree's
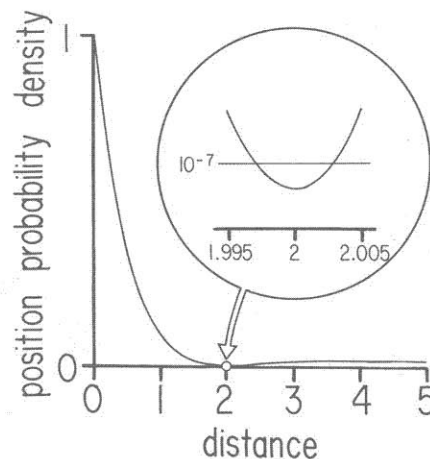

Figure 2. Relativistic position probability density for a 2s state. Probability density expressed in units of its maximum value, radial distance in units of a/Z.

observation (*10*), on the basis of general properties of the spherical harmonics, that the angular dependence of position probability density of the small components is identical with that of the large components, so that we need only consider the two large components. This simplification is equivalent to reducing the Dirac four-component eigenfunctions to the Pauli two-component eigenfunctions.

A few explicit angular functions are given in Table 1. Others can readily be calculated (Appendix). White, in his 1931 paper (*3*) calculated and drew graphs to illustrate all the angular distributions up through the g states ((*3*), pp. 516–517). The qualitative features can be summarized as follows:

(*a*) Orbitals with the same value of j and m have the same angular distribution. Thus the $p_{1/2}$ distribution is spherically symmetrical, like the $s_{1/2}$. The pair of $d_{3/2}$ orbitals has the same angular distribution as the pair of $p_{3/2}$. The triplet of $f_{5/2}$ has the same as the triplet of $d_{5/2}$. And so on.

(b) The $s_{1/2}$ distribution is spherically symmetrical. For other states with this lowest possible value of m, namely, $m = 1/2$, the angular distribution is stretched out along the z axis but has no nodes. The $p_{3/2}$, $m = {}^1/_2$ state, for example, has an angular dependence of $\cos^2 \theta + {}^1/_3$, so it more resembles a dog-bone than two touching ellipsoids. The angular distribution and the corresponding contour map of position probability density for the $2p_{3/2}$, $m = {}^1/_2$ state are shown in Figure 3.
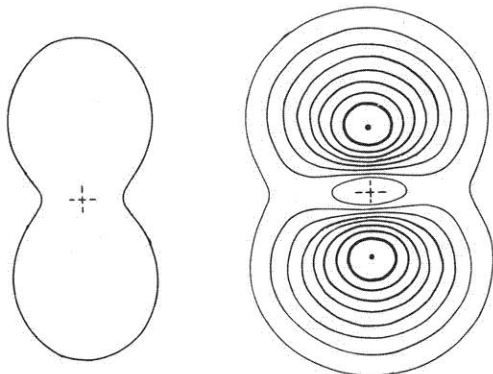

Figure 3. Left, angular factor of the position probability density for the $2p_{3/2}$, $m = {}^1/_2$ state of an isolated atom. Right, probability contours for that state, counting downward at 10% increments from its maximum value. When the probability density is 25% or less of its maximum value, there is no discontinuity between the regions of space.

(c) The state with the highest possible m value for its value of j, such as the $p_{3/2}$, $m = {}^3/_2$, the $d_{5/2}$, $m = {}^5/_2$ the $f_{7/2}$, $m = {}^5/_2$ states, always has a distribution in the shape of a toroid. A doughnut. No nodes.

(d) The states with m falling between its lowest and highest possible value have distributions resembling two-lobed, three-lobed, etc., toroids, but which never approach zero. No nodes.

In short, the angular dependence of position probability density for an isolated atom may have mild minima, but never has anything even resembling an angular node. This nonexistence of angular nodes does not arise from any consideration so subtle as that of the Dirac small components, but is merely a natural consequence of the correct handling of the angular dependence for an electron with spin. The correct result would be obtained if the calculations were carried through with the Pauli two-component theory. The familiar Schrödinger angular distributions are, then, those for the nonexistent spinless electron.

Let us turn next to the question of the angular distribution for an electron on an atom within a molecule. Here the distinguishing physical circumstance is that the atom is subjected to the intense electrostatic field resulting from the neighboring nuclei, or, if one of the atoms of the environment be paramagnetic, to an intense magnetic field. Chemists have long known that, in most molecules, the orbital angular momentum is "quenched" by the electrostatic or magnetic field, so that they have not used eigenfunctions appropriate to the isolated atom, but linear combinations of eigenfunctions so chosen as to give zero net angular momentum.

We need, then, to look at the Dirac eigenfunctions in intense electrostatic or magnetic fields, i.e., to the limiting cases of Stark effect and Zeeman effect. In such a field, the electron will be in a state approximating a pure spin state—one of the large components will be fully excited, while the other becomes zero to the order of the ratio (fine structure splitting)/(Zeeman or Stark splitting) ((*8*) p. 205, *et seq.*). We seek, then, to form linear combinations of eigenfunctions of a given n and l, such that one of the two large components becomes zero. For the $2p$ orbitals, the large spin-down component is zero for the combinations:

$$\sqrt{{}^2/_3}P_{3/2}, \ m = {}^1/_2 \qquad -\sqrt{{}^1/_3}P_{1/2}, \ m = {}^1/_2$$

$$\sqrt{{}^1/_2}P_{3/2}, \ m = {}^3/_2 \qquad +\sqrt{{}^1/_3}P_{1/2}, \ m = -{}^1/_2$$
$$-\sqrt{{}^1/_6}P_{3/2}, \ m = -{}^1/_2$$

$$\sqrt{{}^1/_2}P_{3/2}, \ m = {}^3/_2 \qquad -\sqrt{{}^1/_3}P_{1/2}, \ m = -{}^1/_2$$
$$+\sqrt{{}^1/_6}P_{3/2}, \ m = -{}^1/_2$$

and the large spin-up is $({}^1/_{32})^{1/2} \ r \ e^{-r/2}$ multiplied by, respectively, $\cos \theta$, $\sin \theta \cos \phi$, and $i \sin \theta \sin \phi$. But these are just the familiar p_z, p_x, and p_y. So we show that it is possible to construct Schrödinger-type orbitals, provided the requirement be dropped that j and m be good quantum numbers. Now, the choice of linear combination which has made one of the large components vanish does not make either of the small components vanish. Even in the nodal plane of the large component, the small components contribute a position probability density which is non-zero (except possibly at isolated points).

In summary, the situation with regard to angular nodes of an atom within a molecule is much the same as that with regard to the radial nodes: at the angular Schrödinger "nodes" the relativistic treatment again leads to a residual probability density of the order of $(Z/137)^2 \, r^{2n-2} \, e^{-2r/n}$

Circulating Current and the Electron Spin

It is sometimes forgotten that every quantum-mechanical problem, relativistic or not, has two solutions: a position probability density and a probability current which need not vanish, even in the stationary state, but must then satisfy the condition that its divergence be zero, i.e., that probability be locally conserved. In a Dirac atom, the probability current does not van-

ish. Its three space components are given, in units of c, by

$$\psi^* \alpha_x \psi$$
$$\psi^* \alpha_y \psi$$
$$\psi^* \alpha_z \psi$$

With the aid of the Dirac velocity operators (*vide supra*) it is straightforward to evaluate the probability current. Hartree (*10*) was the first to do so explicitly, showing that the x-component is proportional to $\sin \phi$, the y-component proportional to $-\cos \phi$ with the same coefficient of proportionality, and the z-component is zero. This clearly represents a nonvanishing probability current circulating about the axis of z. Table 2 gives the tangential magnitude of this circulating current for the atomic states listed in Table 1.

Table 2. Magnitude of the Circulating Probability Current, in Units of $\alpha c Z/\pi$	
$1s^{1/2}$	$e^{-2r} \sin \theta$
$2s^{1/2}$	$(1/8)(1 - r/2)(1 - r/4)e^{-r} \sin \theta$
$2p^{1/2}$	$(1/32)\, r\, (1 - r/6)\, e^{-r} \sin \theta$
$2p^{3/2}, \ m = \ ^3/_2$	$(1/128)\, r^2 e^{-r} \sin^3 \theta$
$2p^{3/2}, \ m = \ ^1/_2$	$(1/128)\, r^2 e^{-r} \sin \theta \ (\cos^2 \theta + \ ^1/_3)$

Two features of the circulating current are worth comment: Its radial dependence is always that of the product fg, so that the circulating current reverses direction wherever either f or g passes through zero. Its angular dependence is always that of the probability density itself multiplied by $\sin \theta$, so that there are no angular reversals of the current.

Hartree went a step farther (*10*). He worked out the general expression for the magnetic moment which results from such a circulating probability current. The procedure is as follows: multiply the probability current by $-e$ to convert it to electric current; multiply by its axial distance ($r \sin \theta$) and divide by 2, which according to classical electrodynamics gives the magnetic moment; divide by c to convert to electromagnetic units; and sum over all space. Hartree carried out the calculation to obtain the following expression

$$\text{magnetic moment} = (e\alpha a/2) \frac{j + \ ^1/_2}{l + \ ^1/_2} \, m$$

The first factor in this expression is just the Bohr magneton. The second is the Landé splitting factor. The third is the magnetic quantum number. Taken together, they give correctly all the magnetic levels of the electron in an atom. In other words, the circulating current is exactly enough to account for all the magnetic properties of an electron in an atom.

This remarkable result deserves greater fame than it has. A number of textbook authors have asserted, without bothering to give their evidence, that the "spin" of an electron is to be thought of as a rotation of the electron about an axis through it, rather like the daily rotation of the earth around the axis between its North Pole and South Pole. As we see, the evidence contradicts that statement. Inasmuch as the magnetic properties of the electron are already exactly accounted for by its circulational motion, any additional effect arising from its rotating around an axis through it would de-

stroy the agreement with experiment. If a physical visualization of "spin" be needed, it is perhaps better to think of it as the lower limit of circulational motion below which the electron will not drop. The electron appears to be a particle which doesn't like to move in straight lines—it insists on moving in helical spirals wherever it goes.

How can an electron with a fixed total angular momentum j give rise to several different possible values of magnetic moment? The old answer, the "vector model," was that there was a total magnetic moment corresponding to the total angular momentum, but that only quantized values of its projection along the z axis were observable. Hartree (*10*) already in 1929 had complained about such an interpretation. The probability current gives both a qualitative and a quantitative explanation. As has already been mentioned, the circulating current passes through zero and reverses its sign wherever g or f is zero. Thus the circulating current does not reverse for a $1s$ state. It reverses at $r = 2$ and again reverses at $r = 4$ for a $2s$ state. It reverses once at $r = 6$ in a $2p^{1/2}$ state. And so on. These various reversals serve to cancel one another's magnetic effects, and so lead to various possible intermediate magnetic moments.

The *Zitterbewegung* Approach

There is another way of looking at the relativistic problem which, although mathematically equivalent to Dirac's, puts it in quite a different perspective.

It is possible to solve for the eigenvalues of the Dirac velocity operators, which turn out to be ± 1, i.e., the instantaneous value of any one component of the electron's velocity is either $+c$ or $-c$. The frequency of the motion with this velocity is, however, at least $2mc^2/\hbar$ and thus very high ((*2*), p. 205, *et seq.*), so that the average amplitude of the motion is less than $^1/_{137}$ of a Bohr radius. The electron is thus executing a kind of motion which Schrödinger called "jitter-movement," *Zitterbewegung* (*11*), a very rapid motion of very small amplitude, periodic for a free electron and almost periodic for a bound electron, superimposed on whatever slow motion it may be executing.

In 1950, Foldy and Wouthuysen set out to find a mathematical representation of the electron's eigenfunction that did not have Dirac's small components. And they succeeded ((*12*), p. 51 *et seq.*; *13*, p. 152 *et seq.*; (*2*), p. 206). But their function turned out not to represent the probability of an electron's being at a position, but instead the probability of the center of gravity of its *Zitterbewegung* being at a position. In the Foldy-Wouthuysen representation, there can indeed be nodes. However, this only means that the center of gravity of the *Zitterbewegung* cannot sit right on a node; it can sit nearby, and the *Zitterbewegung* carry the electron across.

One advantage of the Foldy-Wouthuysen approach is its generality. It shows us, without our having to solve every separate problem in the Dirac way, that there cannot ever be any true nodes in the position probability density.

Another advantage is that it serves as a bridge between the rigorous Dirac approach and the spin-orbit approach so widely used in the theory of atomic spectra. As the reader will recall, spin angular momentum and

orbital angular momentum, taken separately, had to be discarded from the Dirac theory because they are not constants of motion. In the Foldy-Wouthuysen representation, they now reappear in the form of "mean spin angular momentum" and "mean orbital angular momentum." The Foldy-Wouthuysen Hamiltonian can be expanded in powers of αZ, and when this is done as far as the second order, two small energy terms appear: One of them has the form of a mean-spin-mean-orbit interaction, and corresponds correctly to Dirac's fine-structure shift. The other is a contact term which vanishes except for s states, and corresponds correctly to Dirac's relativistic shift of s states.

The Electron in a Box

The Dirac treatment of an electron in a one-dimensional "box" (i.e., potential well with infinitely high walls) is given in detail in Sherwin's textbook ((7), p. 301 et seq.; p. 373, et seq.). The problem is somewhat simplified by the circumstance that the electron can be in a pure spin state, i.e., we need only consider one large and one small component.

The reader will recall that the energy levels of a non-relativistic electron in a box are given by

$$E_n = n^2 h^2 / 8mL^2$$

and the eigenfunctions by

$$\psi_n = (2/L)^{1/2} \sin n\pi x/L$$

Let us write p for the absolute value of the momentum of the electron, namely $nh/2L$. Then p/m is its speed, and p/mc its speed compared to the speed of light. The energy levels of the relativistic electron are then slightly more negative than the nonrelativistic, each by a fraction of its own value equal to $1/4\ (p/mc)^2$. Compare the corresponding result for the energy levels of an atom, given in the caption to Figure 1.

The Dirac eigenfunctions, with normalization correct to first order in p/mc, are

$$\psi_n = (2/L)^{1/2} \begin{bmatrix} 1/2 \sin n\pi x/L \\ 1/2 i(p/mc)\,\cos n\pi x/L \end{bmatrix}$$

so that wherever the large component has a node, the small component remains nonzero. Thus there are no nodes in the position probability density of an electron in a box, either.

Other Particles

The other two constituents of ordinary matter, the proton and the neutron, are, like the electron, spin $1/2$ particles that obey the Dirac equation. Consequently, there are no nodes in the position probability density for any ordinary matter. It may be mentioned that the circulating probability current does not account for the magnetic moment of the proton entirely, nor of the neutron at all.

Discussion of the other elementary particles of physics would carry us too deeply into relativistic quantum field theory. A general principle can, however, be stated. Any particle of finite rest mass and spin j requires a theory of $4j + 2$ components to describe it. If the particle has zero rest mass, then any process by which it is liberated leaves half the components unexcited, so that only $2j + 1$ components are required. The photon, a massless particle of spin 1, requires a 3-component theory. The neutrino, a massless particle of spin $1/2$, can be described by a 2-component theory, a slightly simplified version of the Dirac treatment.

Appendix

The general expression for the Dirac eigenfunctions of a hydrogenlike atom is the following

$$\psi = \sqrt{N}\begin{bmatrix} g\sqrt{\dfrac{l + 1/2 \pm m}{2l + 1}}\ Y_{l,m-1/2} \\[2ex] \mp g\sqrt{\dfrac{l + 1/2 \mp m}{2l + 1}}\ Y_{l,m+1/2} \\[2ex] -if\sqrt{\dfrac{2j - l + 1/2 \mp m}{4j - 2l + 1}}\ Y_{2j-l,m-1/2} \\[2ex] -if\sqrt{\dfrac{2j - l + 1/2 \pm m}{4j - 2l + 1}}\ Y_{2j-l,m+1/2} \end{bmatrix}$$

where N is a normalization factor, the symbol $\pm$ denotes the sign of $j - l$, g and f are radial factors defined below, and Y is the indicated spherical harmonic ((8), p. 5).

The large radial factor g and the small radial factor f are, to first order in αZ, given by

$$g = e^{-r/n} \times \{r^{n-1}[n + 1/2 \pm l \pm 1/2] -$$
$$r^{n-2}(n/2)[n + 1/2 \pm l \pm 1/2 - 1][n - l \mp 1] \times$$
$$[n + l \pm 1]/1! + r^{n-3}(n/2)^2[n + 1/2 \pm l \pm 1/2 - 2] \times$$
$$[(n - l \mp 1)(n - l \mp 1 - 1)] \times$$
$$[(n + l \pm 1)(n + l \pm 1 - 1)]/2! - \ldots\}$$

$$f = -\frac{\alpha Z}{2n}\, e^{-r/n} \times \{r^{n-1}[n + 1/2 \pm l \pm 1/2] \times$$
$$-r^{n-2}(n/2)[n + 1/2 \pm l \pm 1/2 + 1][n - l \mp 1] \times$$
$$[n + l \pm 1]/1! + r^{n-3}(n/2)^2[n + 1/2 \pm l \pm 1/2 + 2] \times$$
$$[(n - l \mp 1)(n - l \mp 1 - 1)] \times$$
$$[(n + l \pm 1)(n + l \pm 1 - 1)]/2! - \ldots\}$$

where r is measured in units of a/Z and each series terminates with the zeroth power of r. If these radial series are evaluated to the order of $\alpha^2 Z^2$ or higher, various of the factors of the coefficients become slightly different from integers; but the difference is so small that it can be ignored for any ordinary purpose (cf. (8), p. 69).

The normalization factor N can be worked out in general terms ((8), p. 69), but it is handier merely to require that $N\displaystyle\int_0^\infty (g^2 + f^2)r^2 dr$ be equal to unity.

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