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Joseph O. Hirschfelder, Charles J. Goebel,

and Ludwig W. Bruch

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QUANTIZED VORTICES AROUND WAVEFUNCTIONS NODES[*]

Joseph O. Hirschfelder

Theoretical Chemistry Institute

and

Charles J. Goebel and Ludwig W. Bruch

Department of Physics

The University of Wisconsin

Madison, Wisconsin   53706

ABSTRACT

Quantized vortices can occur around nodal points in wavefunctions. This fact, discovered by Dirac (1931) but little noted since, is rederived here and examples are discussed. The derivation depends only on the wavefunction being single valued, continuous, and having continuous first derivatives. Since the derivation does not depend upon the dynamical equations, the quantized vortices are expected to occur for many types of waves (i.e. electromagnetic, acoustic, etc.). Such vortices have appeared in the calculations (McCullough and Wyatt, Kuppermann) of the $H + H_2$ molecular collisions and play a role in the chemical kinetics. In a companion paper, it is shown that quantized vortices occur when optical waves are internally reflected from the face of a prism or particle beams are reflected from potential energy barriers.

McCullough and Wyatt[1] observed what they termed "the quantum whirlpool effect" when they integrated the quantum mechanical equations of motion for the collinear collision of a hydrogen atom and a hydrogen molecule. This was a vortex in the flux around a node in the wavefunction of the composite system moving on a potential energy surface. From a classical point of view, it is surprising that the flux might go around in closed loops when the potential surface does not have a dimple. Since the vortex occurred near the saddle point in the potential surface, the whirlpool effect may be important in the chemical kinetics. (The vortex produces multiple crossings of the activated state and thereby lessens the steric factor in the theory of absolute reaction rates.) Recent unpublished calculations of Kuppermann, and also Wyatt, are said to show interesting variations in the behaviour of the vortex with energy, especially near resonances.

In the preceding paper,[2] vortices are found surrounding nodes in the wavefunction describing an optical beam internally reflected at a prism face. Or, with another interpretation of the mathematical treatment, vortices are found surrounding nodes in the wavefunction describing the reflection of particles impinging upon a square potential barrier. Clearly, the occurrence of vortices is a very general phenomenon. These quantum whirlpools would not be evident from classical trajectory calculations since they result from the interference of waves.

Here we present a rederivation of a fact discovered in 1931 by Dirac:[3] Vortices are to be expected around the nodal points of

wavefunctions and these vortices are quantized. We use the term "wavefunction" to denote the spin-free component of a wavefunction. The proof is elementary and depends only upon the requirement that the wavefunction be single-valued and continuous and its first derivatives be continuous. There is no requirement that the wavefunction satisfy any particular dynamical equations. Thus, the same type of quantized vortices should occur in electromagnetic, acoustic, hydrodynamic, and other types of wave mechanics. Our formulation is expressed in terms of Schrödinger quantum mechanics, but the equations and examples apply equally well to these other types of waves provided that the meanings and values of the constants $\hbar$ and m are changed appropriately.

Our discussion of nodes and vortices also applies to superfluids or superconductors which are characterized by a "macroscopic wavefunction" or amplitude $\Psi(r,t)$. The density ρ and the local mean velocity v are defined in terms of $\Psi(r,t)$ by the same equations as in Schrödinger wave mechanics. However, the superfluids or superconductor Ψ differs from the Schrodinger wavefunction in not satisfying a linear equation (i.e. a linear combination of two solutions Ψ_1 and Ψ_2 is not itself a solution). For superfluids or superconductors, the Madelung[4] type of hydrodynamical formulation of the quantum mechanical equations is convenient, whereas, for Schrödinger wave mechanics, the hydrodynamical formulation has had only limited usefulness up to the present time.

I. DERIVATION

As in the preceding paper,[2] we express an arbitrary Schrödinger wavefunction in the form $\Psi(\underset{\sim}{r},t) = \rho^{1/2} \exp(iS/\hbar)$ where both $\rho^{1/2}$ and S are real. Then the probability density is $\rho = \Psi^*\Psi$ and the phase of Ψ is $S/\hbar$. The number flux is

$$\underset{\sim}{J} = (i\hbar/2m)[\Psi\nabla\Psi^* - \Psi^*\nabla\Psi] , \qquad (1)$$

where m is the mass of the particles. The Madelung-Landau-London definition of the local mean velocity is

$$\underset{\sim}{v} = \underset{\sim}{J}/\rho = (1/m) \, Im[\nabla\Psi/\Psi] = \nabla S/m . \qquad (2)$$

The fluid flow is irrotational around points where Ψ is not equal to zero, since there $\nabla \times \underset{\sim}{v} = \nabla \times \nabla S/m = 0$. However, around nodes in the wavefunction, $\underset{\sim}{v}$ becomes indeterminate since both $\underset{\sim}{J} = 0$ and $\rho = 0$. It is this indeterminancy which leads to the possibility of vortex motion around nodes.

Both Ψ and $\nabla\Psi$ are required to be continuous and single valued everywhere except that at points where the potential energy is infinite, Ψ remains continuous but $\nabla\Psi$ may be discontinuous. It follows that we can, and do, choose $\rho^{1/2}$ so that it is everywhere continuous and $\nabla\rho^{1/2}$ so that it is continuous except at points where the potential energy is infinite. (Note that this choice implies a restriction on the value of S since Ψ remains unchanged if the

sign of $\rho^{1/2}$ is changed at the same time that π is added to the value of $S/\hbar$.) When $\Psi = 0$, neither $S/\hbar$ nor ∇S are well defined. At all points where Ψ does not vanish, ∇S is well defined; and at all points where Ψ is not zero, $S/\hbar$ is defined up to an integer multiple of 2π .

The existence of vortices can be explained in the following manner: If S_p is the principal value of S and n is an integer then $S_p/\hbar$ and $(S_p/\hbar) + 2\pi n$ are indistinguishable since $\exp[iS_p/\hbar] = \exp[i(S_p/\hbar) + 2\pi ni]$. Because of this lack of uniqueness of $S/\hbar$, the line integral of $\underset{\sim}{v}$ between two points r_1 and r_2 is

$$\int_{\underset{\sim}{r}_1}^{\underset{\sim}{r}_2} \underset{\sim}{v} \cdot d\underset{\sim}{r} = m^{-1} \int_{\underset{\sim}{r}_1}^{\underset{\sim}{r}_2} \nabla S \cdot d\underset{\sim}{r} = m^{-1}[S_p(\underset{\sim}{r}_2) - S_p(\underset{\sim}{r}_1)] + 2\pi\hbar/m)n . \quad (2)$$

The value of n depends upon the path which is followed in going from r_1 to r_2 . In following along any particular path (not passing through a node) ∇S is well defined so that the value of the line integral is unique. If two paths between r_1 and r_2 lie close together and neither passes through a node, then the value of the corresponding line integrals must be the same. One might expect that these two line integrals might differ slightly since ∇S can be expected to have slightly different values at comparable points along the two paths. However, according to Eq. (3), the values of these two line integrals can differ only by integer multiples of $(2\pi\hbar/m)$ and, hence, cannot differ slightly. Thus, we reach the conclusion that any two line integrals between the same end points have the same

value provided that one path can be deformed into the other without intersecting any region where $\Psi = 0$. Furthermore, if the end points are coincident, so that the paths are closed loops, the location of the end point is irrelevant and Eq. (3) becomes

$$\oint \underset{\sim}{v} \cdot d\underset{\sim}{r} = (2\pi\hbar/m)n . \tag{4}$$

For any two closed loops, the value of the line integral is the same provided that the loops can be deformed into one another without intersecting any point where $\Psi = 0$. For example, if a closed loop does not enclose any nodal points, then the closed loop can be deformed by shrinking it into a circle of radius zero without changing the value of the line integral. In such a case, the value of the line integral must be zero, or $n = 0$, in agreement with our previous conclusion that the fluid flow is irrotational except in the vicinity of a nodal point. Conversely, there can be no angular velocity around a point for which Ψ does not vanish. Atomic wavefunctions provide a good example: Only S-states have ρ nonvanishing at the nucleus.

If the closed loop encloses a node in the wavefunction at the point $\underset{\sim}{r}_0$, then the value of $|n|$ depends upon the behaviour of the wavefunction in the vicinity of the node. Let us take the line integral over a circular path of radius q with $\underset{\sim}{r}_0$ as center. The circular path is taken in an xy-plane where $x = q \cos\phi$ and $y = q \sin\phi$. The values of Ψ and S at a point on the path

corresponding to the angle ϕ can be designated as $\Psi(\phi)$ and $S(\phi)$ respectively. Here

$$S(\phi)/\hbar = n'\pi + \tan_p^{-1}\{Im[\Psi(\phi)]/Re[\Psi(\phi)]\} , \qquad (5)$$

where n' is an integer and $\tan_p^{-1}$ is the principle value of the arc tangent. The $\tan[S(\phi)/\hbar]$ becomes discontinuous at a set of points $\phi = \phi_k$ where

$$Re[\psi(\phi_k)]/Im[\Psi(\phi_k)] = 0 . \qquad (6)$$

Let s_k be the sign of $\tan[S(\phi_k - \epsilon)/\hbar]$ where ϵ is a small angle, then if $S(\phi)$ is to remain continuous, each time that ϕ passes through a ϕ_k for which s_k is positive, n' increases by one; and every time it passes through a ϕ_k for which s_k is negative, n' decreases by one. Thus, from Eqs. (3) and (4),

$$\oint \underset{\sim}{v}\cdot d\underset{\sim}{r} = (\hbar/m)[S(2\pi) - S(\phi)] = (\pi\hbar/m) \sum_k s_k 1 = (2\pi\hbar/m)n . \quad (7)$$

Here the summation is over all of the ϕ_k between $\phi = 0$ and 2π. Since Ψ is single-valued, there is an even number of ϕ_k's so that n is an integer.

The existence of quantized vortices around nodes is well known for analytical functions in the complex plane. However, it is surprising that the same sort of behaviour also applies to complex

wavefunctions in an arbitrary number of dimensions D provided that they are single valued, continuous, and have continuous first derivatives. As we have seen, there is associated with each node of Ψ a magnitude of circulation $|n|$ corresponding to the circulation around a simple loop which encloses this particular node and no other node. The sign of the circulation depends upon the direction in which one progresses around the loop. Of course, the circulation $|n|$ of this node can be nonvanishing only if the node is topologically equivalent to a (D-2)-dimensional subspace without a boundary. Otherwise, the wavefunction could not satisfy its single-value and continuity requirements. For instance, in three dimensions, a node with circulation must be a ring, an endless ("vortex") line, or else a ribbon or rod which is topologically equivalent (can be shrunk) to an endless line--a line with end points or a single point would not suffice.

The wavefunction can be expanded in a many-dimensional Taylor's series about a nodal point r_0 . Then, if the node is of the g-th order so that the first nonvanishing term involves the g-th order of the coordinates, it is easy to prove (by examining the possible number of the ϕ_k's) that $|n|$ must be less than or equal to g . The first order nodes occur most frequently. Near a first order nodal point r_0 , the wavefunction can be expanded in the form

$$\Psi = [\alpha + i\beta] \cdot (r - r_0) + [\gamma + i\delta] : (r - r_0)(r - r_0) + \dots , \qquad (8)$$

where the α, β, γ, and δ are real and constant. In order that the node be of the first order, either α or β must be nonvanishing. The second order term (involving γ and δ) and the higher order terms then do not affect the value of n . If α and β are parallel so that $\beta = c\alpha$, this would be an example of a (D-1)-dimensional node since, to the first approximation, the only nonvanishing configurations of $r - r_0$ lie along a line in the direction of α . Since $\tan(S/\hbar) = c$, it is obvious that $n = 0$ which is confirmation of the theorem that a (D-1)-dimensional node is topologically unsuited to support a vortex. The same argument would apply to the case where either α or β were zero. If α and β are not parallel, we can choose the x-axis to be in the direction of α and choose the y-axis so that β lies in the xy-plane. Such a node is (D-2)-dimensional since the only nonvanishing configurations of $(r - r_0)$ lie in the plane defined by α and β . For this case, $\tan(S/\hbar) = (\beta_x/\alpha_x) + (\beta_y/\alpha_x)\tan\phi$. Thus, there are two values of ϕ for which $\tan(S/\hbar)$ becomes discontinuous, $\phi_1 = \pi/2$ and $\phi_2 = 3\pi/2$, and $s_1 = s_2$ so that either $n = 1$ or $n = -1$. If $\nabla\Psi$ is parallel to $\nabla\Psi^*$ in the vicinity of a node, then that node cannot support a circulation. A case of this nature is $\Psi = y \exp(ikx)$. Here $S/\hbar = kq \cos\phi$ so that $\tan(S/\hbar)$ has no discontinuities and $n = 0$.

It is easy to show that in the presence of a magnetic field with a vector potential A , the extra term, $-(e/mc)A$, in v does not

contribute to the value of the line integral provided that the radius q is required to approach zero.

II. EXAMPLE: AN INFINITE FIELD OF REGULARLY SPACED VORTICES

An infinite number of vortices with $m = 1$ or $m = -1$ appear at regular spacings when two plane waves, Ψ_1 and Ψ_2, having the same energy $E = k^2\hbar^2/2\mu$ but corresponding to motions in different directions, are reflected from a plane wall so that their reflected wavefunctions are Ψ_1' and Ψ_2'. Thus, the total wavefunction for the system is $\Psi = \Psi_1 + \Psi_2 + \Psi_1' + \Psi_2'$. For simplicity, let the plane wall be the surface $x = 0$ and the incoming wavefunctions be

$$\Psi_1 = i \exp[-ik(x \cos\phi_1 + y \sin\phi_1)]$$

and (9)

$$\Psi_2 = i \exp[-ik(x \cos\phi_2 + y \sin\phi_2)] ,$$

where ϕ_1 and ϕ_2 are constants. The reflected wavefunctions are then

$$\Psi_1' = -i \exp[ik(x \cos\phi_1 - y \sin\phi_1)]$$

and (10)

$$\Psi_2' = -i \exp[ik(x \cos\phi_2 - y \sin\phi_2)] .$$

For notational convenience, let $a = k \cos\phi_1$, $b = k \sin\phi_1$, $\alpha = k \cos\phi_2$, and $\beta = k \sin\phi_2$. Then,

$$\Psi = 2\sin(ax)\exp(-iby) + 2\sin(\alpha x)\exp(-i\beta y) \qquad (11)$$

so that there are four conditions under which $\Psi = 0$,

(1). $\cos[(b-\beta)y_0] = 1$ and $\sin[(a+\alpha)x_0/2] = 0$ so that

$$x_0 = 2\pi j/(a+\alpha), \quad y_0 = 2\pi k/(b-\beta) ;$$

(2). $\cos[(b-\beta)y_0] = -1$ and $\sin[(a-\alpha)x_0/2] = 0$ so that

$$x_0 = 2\pi j/(a-\alpha), \quad y_0 = \pi(1+2k)/(b-\beta) ;$$

(3). $\cos[(b-\beta)y_0] = 1$ and $\cos[(a-\alpha)x_0/2] = 0$ so that

$$x_0 = \pi(1+2j)/(a-\alpha), \quad y_0 = 2\pi k/(b-\beta) ;$$

(4). $\cos[(b-\beta)y_0] = -1$ and $\cos[(a+\alpha)x_0/2] = 0$ so that

$$x_0 = \pi(1+2j)/(a+\alpha), \quad y_0 = \pi(1+2k)/(b-\beta) ,$$

where the constants j and k are either zero or a positive or negative integer.

ACKNOWLEDGEMENTS

REFERENCES

1. E. A. McCullough, Jr. and R. E. Wyatt, J. Chem. Phys. $\underline{54}$, 3578 (1971). See especially p. 3584 and Figs. (13) and (16).

2. J. O. Hirschfelder, W. E. Palke, and A. C. Christoph, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-514 (1974).

3. P. A. M. Dirac, Proc. Roy. Soc. $\underline{A133}$, 60 (1931). See also, I. and Z. Biaynicki-Birula, Phys. Rev. $\underline{D3}$, 2410 (1971).

4. E. Madelung, Zeit. Phys. $\underline{40}$, 322 (1926).