

Limits of Error for the Electron Density, Spin Density, and Atomic Form Factor in Quantum-Mechanical Calculations*

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Explicit formulas are given for the limits of error at an arbitrary point in the electron density, spin density, and form factor derived from an approximate wave function. In the derivation extensive use is being made of some previous results by Kinoshita. The main treatment is preceded by a short discussion of some of the more mathematical aspects of the problem, and a simple numerical example is given in the last paragraph.

1. INTRODUCTION

THE properties of an atom in its ground state can be calculated from the solution of the time-independent Schrödinger equation

$$H\psi_0 = E_0\psi_0,$$

where E_0 is the lowest eigenvalue of the Hamilton operator H and ψ_0 is the corresponding eigenfunction which depends on the space and spin coordinates of the electrons. Unfortunately, however, the Schrödinger equation is of such a complicated form that, except for the simplest case of the hydrogen atom, it does not seem possible to obtain the exact solution. On the other hand, there are methods available by which approximations to ψ_0 of varying degree of accuracy can be obtained. As more and more refined calculations had been made, at least on small atoms, there has been a continued interest in deriving limits of error for the expectation value of the energy¹ and other quantities² calculated from an arbitrary trial wave function ψ .

The main purpose of this paper is to show that it is possible to derive limits of error for quantities of the type $|\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})|$, where \mathbf{a} is an arbitrary point in three-dimensional Euclidian space, γ_0 is the electron density derived from the exact solution, and γ is an approximate electron density obtained from a trial function ψ . This will be achieved in terms of four quantities; the exact ground state and first excited state energy, the expectation value and the mean square deviation of the energy. The derivation is based largely on ideas to be found in a paper by Kinoshita.³ Kinoshita estimated the error in the relativistic corrections for a

helium atom trial wave function. This required an estimate of the error in the electron density at the singularities of the potential. It will be shown here that these results can be generalized to apply on one hand to an arbitrary point in space and on the other hand to any atomic system. From this, one will be able to conclude that if a wave function gives good energy and small mean square deviation for the energy the electron density will be a good approximation to the exact density, everywhere, even in those regions of space which from the point of view of energy may seem unimportant.

It is well known that the state vectors which describe a quantum-mechanical system are elements of the Hilbert space of quadratically integrable functions.⁴ These functions form a Hilbert space only if the integration is understood in the sense of Lebesgue (von Neumann⁴). From this it follows that two wave functions, which differ on a set of zero measure (e.g., set of isolated points), describe the same physical situation. Therefore, it may at first sight seem surprising that one can meaningfully discuss the value of the electron density in a given point. It will be discussed in the next introductory chapter how the ambiguity on a set of zero measure can be removed if not only ψ but also $H\psi$ belongs to the Hilbert space of quadratically integrable functions. This requirement seems reasonable both from the mathematical and physical standpoint. The preparatory mathematical considerations of the next section are, however, not strictly necessary for the understanding of the subsequent main discussion.

2. PRELIMINARY DIGRESSION

Let us consider an atomic system with N electrons and with nuclear charge Z . Let \mathbf{r}_i and ζ_i denote the position and spin coordinates of the i th electron and let \mathbf{x}_i stand for the collection of \mathbf{r}_i and ζ_i . The Hilbert space associated with this system will be denoted by $L_A^2(\mathbf{x}_1, \dots, \mathbf{x}_N)$ defined as the set of all functions $\phi(\mathbf{x}_1, \dots, \mathbf{x}_N)$ which are antisymmetric in the variables \mathbf{x}_i and satisfy the condition

$$(\phi, \phi) = \int |\phi(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_N d\zeta_1 \dots d\zeta_N < \infty. \quad (1)$$

⁴ J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1955).

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¹ See, e.g., G. Temple, *Proc. Roy. Soc. (London)* **A119**, 276 (1928); D. H. Weinstein, *Proc. Natl. Acad. Sci. U. S. A.* **20**, 529 (1934); A. F. Stevenson and M. F. Crawford, *Phys. Rev.* **54**, 375 (1938); T. Kato, *J. Phys. Soc. Japan* **4**, 334 (1949); A. Fröman and G. G. Hall, *J. Mol. Spectr.* **7**, 410 (1961); G. L. Caldov and C. A. Coulson, *Proc. Cambridge Phil. Soc.* **57**, 341 (1961).

² For example V. M. Buimistrov, *Soviet Phys.—JETP* **8**, 812 (1959); P. O. Löwdin, *Ann. Rev. Phys. Chem.* **11**, 107 (1960); and H. Preuss, *Z. Naturforsch.* **16a**, 598 (1961).

³ T. Kinoshita, *Phys. Rev.* **115**, 366 (1959).

Since the set of Riemann integrable functions do not form a Hilbert space but only a linear vector space, the integration over \mathbf{r}_i is in the sense of Lebesgue, whereas the integration over the spin variable ζ_i denotes summation. Two functions which differ on a set of zero measure (zero measure in $3N$ -dimensional Euclidian space⁵) are to be considered identical. The Hamilton operator H is given in the form

$$H = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i<j} \frac{1}{r_{ij}}, \quad (2)$$

where the notation is self-explanatory. The operator H , as it stands, is not yet well defined in the mathematical sense. As a start one may define H for functions which have second derivatives everywhere. It was shown by Kato⁶ that, provided the original definition of H is not too restrictive, there is one and only one self-adjoint extension. It is necessary to make this extension in order to have a resolution of the identity belonging to H , i.e., a complete set of eigenfunctions. The linear vector space on which the self-adjoint extension is defined is called the domain of H and it will be denoted by D_H . D_H is a proper subset of L_A^2 , i.e., $D_H \subset L_A^2$. As shown by Kato the domain D_H consists of all functions $\phi \in L_A^2$ which satisfy the condition

$$\int \sum_{i=1}^N P_i^4 |\tilde{\phi}(\mathbf{p}_1, \dots, \mathbf{p}_N, \zeta_1, \dots, \zeta_N)|^2 d\mathbf{p}_1 \dots d\mathbf{p}_N < \infty, \quad (3)$$

where $\tilde{\phi}$ is the Fourier transform of ϕ . This may be written somewhat loosely in the form

$$(K\phi, K\phi) = \|Kf\|^2 < \infty, \quad (4)$$

where K is the kinetic energy operator. It follows from condition (3) that if $\phi \in D_H$ then $H\phi \in \phi_A^2$, that is, $(H\phi, H\phi) < \infty$. Following the suggestion of Kinoshita⁷ we require that an acceptable trial function ψ should satisfy condition (3), i.e., we require not only $\psi \in L_A^2$ but also $H\psi \in L_A^2$. Let us now define the first-order density function $\gamma(\mathbf{r}_1)$ as

$$\gamma(\mathbf{r}_1) = \int |\psi(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N d\zeta_1 \dots d\zeta_N, \quad (5)$$

which is $1/N$ times the probability of finding an electron with arbitrary spin at the position \mathbf{r} . It is a consequence of a lemma by Kato⁶ that if $\psi \in D_H$, $\gamma(\mathbf{r}_1)$ is essentially continuous, i.e., it can be made continuous by changing its value on a set of zero measure.⁸ Here we shall be

interested to estimate the quantity $|\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})|$, where γ_0 is the exact density and \mathbf{a} a fixed point. The ambiguity on zero measure can now be removed by the following argument: In reality one never measures the electron density at a point but only in a small volume, let us say ΔV . It seems, therefore, reasonable to consider instead of $|\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})|$ the quantity

$$\lim_{\Delta V \rightarrow 0, \Delta V \supset \mathbf{a}} \left| \frac{1}{\Delta V} \int_{\Delta V} \gamma_0(\mathbf{r}) d\mathbf{r} - \frac{1}{\Delta V} \int_{\Delta V} \gamma(\mathbf{r}) d\mathbf{r} \right|.$$

Because of the essential continuity of γ_0 and γ , the result is independent of the way the limiting procedure is carried out and of possible discontinuities on a zero measure. This is equivalent to redefining the densities so that they become continuous everywhere. In the following we shall, thus, be able to assume that the densities had been chosen continuous.

3. LIMITS OF ERROR FOR THE ELECTRON DENSITY

Let $\psi(\mathbf{a}_1, \dots, \mathbf{a}_N)$ be an approximate atomic wave function which satisfies conditions (1) and (3). It can always be written in the form

$$\psi = (1 - \eta^2)^{1/2} \psi_0 + \eta f, \quad (6)$$

where ψ_0 is a ground-state eigenfunction to the Hamilton operator H given by Eq. (2) (the ground state may be degenerate), f is a function orthogonal to the ground-state solutions, and η is a constant which can be chosen real and positive. For typographical convenience we assume all three functions to be real. The constant η satisfies the inequality⁹

$$\eta^2 \leq (\lambda - E_0)/(E_1 - E_0), \quad (7)$$

where $\lambda = (H\psi, \psi)$ and E_0, E_1 are the exact ground state and first excited state energies. The inequality

$$\begin{aligned} & |(1 - \eta^2)(A\psi_0, \psi_0) - (A\psi, \psi)| \\ & \leq \eta |(A\psi, f) + (A f, \psi)| + \eta^2 |(A f, f)| \end{aligned} \quad (8)$$

can easily be obtained from Eq. (6) for any linear operator A . If A is self-adjoint and positive definite, the identity $A = (A)^{1/2}(A)^{1/2}$ and Schwartz's inequality allows us to put this in the simpler form

$$\begin{aligned} & |(1 - \eta^2)(A\psi_0, \psi_0) - (A\psi, \psi)| \\ & \leq 2\eta(\psi, A\psi)^{1/2}(f, A f)^{1/2} + \eta^2(f, A f). \end{aligned} \quad (9)$$

Let us now put $A = \delta(\mathbf{a} - \mathbf{r}_1)$, where $\delta(\mathbf{a} - \mathbf{r}_1)$ is the Dirac δ function in the point \mathbf{a} working on the coordinates of electron 1. One thus obtains

$$\begin{aligned} & |(1 - \eta^2)\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})| \\ & \leq 2\eta[\gamma(\mathbf{a})]^{1/2}[\delta(\mathbf{a} - \mathbf{r})f, f] + \eta^2(\delta(\mathbf{a} - \mathbf{r}_1)f, f). \end{aligned} \quad (10)$$

Our aim is to maximize the right-hand side of (10) in terms of E_0, E_1, λ , and σ , where $\sigma = [(H\psi, H\psi) - \lambda^2]^{1/2}$. This

⁵ J. C. Burkill, *The Lebesgue Integral* (Cambridge University Press, New York, 1951).

⁶ T. Kato, *Trans. Am. Math. Soc.* **70**, 195 (1951).

⁷ T. Kinoshita, *Phys. Rev.* **105**, 1490 (1957).

⁸ Incidentally this result is far from trivial. As it is stated by Kato that for $N > 1$ there exist functions which belong to D_H and are still essentially discontinuous, it apparently does not hold for the wave function itself.

⁹ C. Eckart, *Phys. Rev.* **36**, 878 (1930).

will be achieved in two steps. First, it will be shown that the unknown expression $(\delta(\mathbf{a}-\mathbf{r}_1)f, f)$ can be maximized in terms of (Kf, f) and (Kf, Kf) , where K is the kinetic energy operator. Secondly, the integrals (Kf, f) and (Kf, Kf) on their turn are bounded by an expression which contains only the above-mentioned four quantities. Let us, therefore, consider $(\delta(\mathbf{a}-\mathbf{r}_1)f, f)$. By the definition of the δ function

$$(\delta(\mathbf{a}-\mathbf{r}_1)f, f) = (\delta(\mathbf{r}_1)g, g), \quad (11)$$

where

$$g(\mathbf{r}_1, \zeta_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = f(\mathbf{r}_1 + \mathbf{a}, \zeta_1, \mathbf{x}_2, \dots, \mathbf{x}_N),$$

and $\delta(\mathbf{r}_1)$ is the Dirac δ at the origin. The identity

$$\begin{aligned} (\delta(\mathbf{r}_1)g, g) &= \int \delta(\mathbf{r}_1) [g(\mathbf{r}_1, \zeta_1, \mathbf{x}_2, \dots, \mathbf{x}_N)]^2 d\tau \\ &= -\frac{1}{4\pi} \int \frac{1}{r_1} \nabla_1^2 [g(\mathbf{r}_1, \zeta_1, \mathbf{x}_2, \dots, \mathbf{x}_N)] d\tau, \end{aligned} \quad (12)$$

where $d\tau = d\mathbf{r}_1 \cdots d\mathbf{r}_N d\zeta_1 \cdots d\zeta_N$ can be proved by partial integration provided

$$\frac{d^2}{dr_1^2} \int g^2 d\phi_1 d\theta_1 d\zeta_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

exists everywhere except possibly on a set of isolated points.

This leads to the inequality

$$\begin{aligned} |(\delta(\mathbf{r}_1)g, g)| &\leq \frac{1}{2\pi} \left[\int \frac{1}{r_1} g \nabla_1^2 g d\tau \right. \\ &\quad \left. + \left| \int \frac{1}{r_1} (\text{grad}_1 g)^2 d\tau \right| \right]. \end{aligned} \quad (13)$$

The application of some well-known formulas in vector analysis gives

$$\left| \int \frac{1}{r_1} g \nabla_1^2 g d\tau \right| \leq 2(\nabla_1^2 g, \nabla_1^2 g)^{1/2} (g, -\nabla_1^2 g)^{1/2}, \quad (14)$$

and

$$\left| \int \frac{1}{r_1} (\text{grad}_1 g)^2 d\tau \right| \leq (\nabla_1^2 g, \nabla_1^2 g)^{1/2} (g, -\nabla_1^2 g)^{1/2}.$$

(See, e.g., Kinoshita, reference 3.) From this and inequality (13) it follows that

$$|(\delta(\mathbf{r}_1)g, g)| \leq \frac{3\sqrt{2}}{\pi N} \left\{ (Kg, g)(Kg, Kg) \right\}^{1/2}, \quad (15)$$

as

$$(-\nabla_1^2 g, g) = (2/N)(Kg, g)$$

and

$$\nabla_1^2 g, \nabla_1^2 g \leq (4/N)(Kg, Kg).$$

The kinetic energy operator K is invariant under translation by \mathbf{a} and therefore

$$\begin{aligned} |(\delta(\mathbf{a}-\mathbf{r}_1)f, f)| &= |(\delta(\mathbf{r}_1)g, g)| \\ &\leq \frac{3\sqrt{2}}{\pi N} \left\{ (Kf, f)(Kf, Kf) \right\}^{1/2}. \end{aligned} \quad (16)$$

Substitution of this into (10) yields

$$\begin{aligned} |(1-\eta^2)\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})| \\ \leq 2[\gamma(\mathbf{a})]^{1/2} \left\{ \frac{3\sqrt{2}}{\pi N} \eta(Kf, f)^{1/2} \eta \|Kf\| \right\}^{1/2} \\ + \frac{3\sqrt{2}}{\pi N} \eta(Kf, f)^{1/2} \eta \|Kf\|. \end{aligned} \quad (17)$$

The first part of our aim has now been accomplished. $(Kf, f)^{1/2}$ and $\|Kf\|$ are the only unknown quantities in the right-hand side expression. A straightforward generalization of the formulas given by Kinoshita for the helium case gives the upper bounds

$$\begin{aligned} \eta(Kf, f)^{1/2} &\leq Z(N/2)^{1/2} \eta \\ &\quad [Z^2 N \eta^2 / 2 + (\lambda - E_0) + \eta^2 E_0]^{1/2}, \quad (18) \\ \eta \|Kf\| &\leq [\sigma^2 + \lambda^2 - (1 - \eta^2) E_0^2]^{1/2} \\ &\quad + \alpha^{1/2} \eta(Kf, f)^{1/2}, \end{aligned}$$

where α is a numerical constant given by

$$\alpha = [4Z^2 + 2Z(Z-1)(N-1) + N(N-1)^2]. \quad (19)$$

If one introduces the notation

$$\begin{aligned} C &= \frac{3\sqrt{2}}{\pi N} [Z(N/2)^{1/2} \eta + (Z^2 N \eta^2 / 2 + (\lambda - E_0) + \eta^2 E_0)^{1/2}] \\ &\quad \times \{ [\sigma^2 + \lambda^2 - (1 - \eta^2) E_0^2]^{1/2} + \alpha^{1/2} [Z(N/2)^{1/2} \eta \\ &\quad + (Z^2 N \eta^2 / 2 + (\lambda - E_0) + \eta^2 E_0)^{1/2}] \}, \end{aligned} \quad (20)$$

it will follow from inequalities (17) and (18) that

$$|(1-\eta^2)\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})| \leq 2[\gamma(\mathbf{a})]^{1/2} C^{1/2} + C, \quad (21)$$

which leads to the final formula

$$|\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})| \leq \frac{1}{1-\eta^2} \{ 2C^{1/2} [\gamma(\mathbf{a})]^{1/2} + C + \eta^2 \gamma(\mathbf{a}) \}, \quad (22)$$

where C is given by Eq. (20).

We may thus conclude that the error in the electron density $|\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})|$, in any given point \mathbf{a} , is bounded by an expression which depends besides $\gamma(\mathbf{a})$ only on the quantities λ , σ , E_0 , and η . Inequality (7) provides an upper bound for η whereas λ and σ can be calculated from the wave function ψ . As for E_0 and E_1 , one may either use experimental values or else it is possible to give upper and lower bounds by known methods.

It also follows from formula (21) that if a sequence of trial functions converges to the exact solution, i.e., $\|\psi_0 - \psi^{(n)}\| \rightarrow 0$ and if in addition $\|(H - \lambda^{(n)})\psi^{(n)}\| \rightarrow 0$, the convergence to the electron density is uniform.

It is to be noted that these arguments can easily be generalized to apply to a molecular system. The only difference in the final formula would be that now $Z = \sum_{i=1}^n Z_i$, where n is the number of atoms in the system.

A final remark on the spin density should perhaps be made. The spin density at a point \mathbf{a} may be defined as

$$\gamma(\mathbf{a})_{\text{spin}} = \int \delta(\mathbf{r}_1 - \mathbf{a}) \psi^*(\mathbf{x}_1, \dots, \mathbf{x}_N) S_{z_1} \psi(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_1 \dots d\mathbf{x}_N,$$

where the spin matrix S_z , works only on the spin coordinates of electron 1. Since $\|S_z\| = \frac{1}{2}$, it can be shown by using Schwartz's inequality that

$$|\gamma_0(\mathbf{a})_{\text{spin}} - \gamma(\mathbf{a})_{\text{spin}}| \leq \frac{1}{2} \frac{1}{1 - \eta^2} \{2[\gamma(\mathbf{a})]^{1/2} C^{1/2} + C + \eta^2 \gamma(\mathbf{a})\}, \quad (23)$$

where $\gamma(\mathbf{a})$ is again the total electron density and C is given by (20). The spin density plays an important role in the discussion of the hyperfine interaction and the above formula might be of use for testing the reliability of very accurate calculations.

4. LIMITS OF ERROR FOR ATOMIC FORM FACTORS

The form factor is defined, apart from an unimportant numerical factor, as the Fourier transform of the electron density.¹⁰ Let, therefore, $\tilde{\gamma}_0(\mathbf{k})$ and $\tilde{\gamma}(\mathbf{k})$ denote the Fourier transforms of $\gamma_0(\mathbf{r})$ and $\gamma(\mathbf{r})$. The substitution $A = [1/(2\pi)^{3/2}]e^{-i\mathbf{k} \cdot \mathbf{r}_1}$ in inequality (8) leads to

$$\begin{aligned} |(1 - \eta^2)\tilde{\gamma}_0(\mathbf{k}) - \tilde{\gamma}(\mathbf{k})| &\leq \frac{\eta}{(2\pi)^{3/2}} \left\{ \left| \int e^{-i\mathbf{k} \cdot \mathbf{r}_1} \psi f d\tau \right| \right. \\ &\quad \left. + \left| \int e^{i\mathbf{k} \cdot \mathbf{r}_1} \psi f d\tau \right| \right\} + \frac{\eta^2}{(2\pi)^{3/2}} \left| \int e^{-i\mathbf{k} \cdot \mathbf{r}_1} f^2 d\tau \right| \\ &\leq \frac{2\eta}{(2\pi)^{3/2}} \int |\psi| |f| d\tau + \frac{\eta^2}{(2\pi)^{3/2}} \int f^2 d\tau. \end{aligned}$$

As ψ and f are normalized, Schwartz's inequality gives

$$|(1 - \eta^2)\tilde{\gamma}_0(\mathbf{k}) - \tilde{\gamma}(\mathbf{k})| \leq \frac{1}{(2\pi)^{3/2}} (2\eta + \eta^2),$$

¹⁰ See, e.g., R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1955).

TABLE I. Calculated values of $(C')^{1/2}$, C' , and η_{max}^2 for helium atom wave functions.*

No. of parameters	$-\lambda$	σ^2	η_{max}^2	$2(C')^{1/2}$	C'
6	2.903 24	0.016 90	0.000 485	0.40	0.040
18	2.903 715	0.000 922	0.000 013	0.060	0.000 906
38	2.903 722	0.000 115	0.000 004	0.032	0.000 256

* The values of $-\lambda$ and σ^2 were taken from Table II in reference 7.

which can also be written in the form

$$|\tilde{\gamma}_0(\mathbf{k}) - \tilde{\gamma}(\mathbf{k})| \leq \frac{1}{1 - \eta^2} \left[\frac{1}{(2\pi)^{3/2}} (2\eta + \eta^2) + \eta^2 |\tilde{\gamma}(\mathbf{k})| \right]. \quad (24)$$

Moreover, since

$$|\tilde{\gamma}(\mathbf{k})| \leq \frac{1}{(2\pi)^{3/2}} \int \gamma(\mathbf{r}) d\mathbf{r} = \frac{1}{(2\pi)^{3/2}},$$

we have

$$|\tilde{\gamma}_0(\mathbf{k}) - \tilde{\gamma}(\mathbf{k})| \leq \frac{2}{(2\pi)^{3/2}} \frac{\eta}{1 - \eta}. \quad (25)$$

The last two inequalities might be useful for estimating the accuracy of the form factors used in crystallography.

5. NUMERICAL EXAMPLE

Here we shall illustrate the use of formula (22) by applying it to the helium atom. For helium $Z = 2$, $N = 2$ and so we have

$$|\gamma_0(\mathbf{a}) - \gamma(\mathbf{a})| \leq \frac{1}{1 - \eta_{\text{max}}^2} \{2(C')^{1/2} [\gamma(\mathbf{a})]^{1/2} + C' + \eta_{\text{max}}^2 \gamma(\mathbf{a})\}, \quad (26)$$

where

$$\begin{aligned} C \leq C' &= \frac{3}{2\pi} \frac{1}{\sqrt{2}} \{2\eta_{\text{max}} + [(4 + E_0)\eta_{\text{max}}^2 + (\lambda - E_0)]^{1/2}\} \\ &\quad \times \{[\sigma^2 + \lambda^2 - (1 - \eta_{\text{max}}^2)E_0^2]^{1/2} \\ &\quad + (44)^{1/2} [2\eta_{\text{max}} + ((4 + E_0)\eta_{\text{max}}^2 + (\lambda - E_0))^{1/2}]\} \end{aligned}$$

as

$$0 \leq \eta^2 \leq \eta_{\text{max}}^2 = (\lambda - E_0)/(E_1 - E_0).$$

Table I lists the values of C' , $\sqrt{2}(C')^{1/2}$ and η_{max}^2 for a set of wave functions containing 6, 18, and 38 variational parameters, respectively. For the exact ground state and first excited state energies $E_0 = -2.903 725$ a.u. (atomic units) and $E_1 \approx -2.146$ a.u. were used (reference 3).

The figures in Table I indicate that for those regions of \mathbf{a} in which $\gamma(\mathbf{a})$ is appreciable it is the $2(C')^{1/2}[\gamma(\mathbf{a})]^{1/2}$ term which is the most important in the inequality. The

error for a given $\gamma(\mathbf{a})$ tends to zero as $\mathbf{a} \rightarrow \infty$ whereas the error limit converges to a nonvanishing constant. The accuracy of these limits is difficult to assess and moreover, since formula (22) holds for all values of \mathbf{a} , if a given $\gamma(\mathbf{a})$ is known to be a good approximation to $\gamma_0(\mathbf{a})$ in some regions of space, the actual error in this region may be expected to be much less than that given by inequality (22). If $\gamma(\mathbf{a})$ is obtained through the variation principle, it is likely to be accurate near the singularities of the potential and, consequently, in such a case, formula (22) is likely to overestimate consider-

ably the error near the nuclei. All this, however, does not impair our general conclusions as stated in the introduction.

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Regge Trajectories and Elementary Poles*

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Elementary poles are introduced as poles of physical partial wave amplitudes $F_l(s)$ which are not present in the analytic interpolating function $F(s, \lambda)$. It is shown that $F_l(s) = F(s, l)$ for $l > 1$, and that all particles with spin larger than one must be members of Regge trajectories; only bosons are considered explicitly. Additional restrictions are discussed which would make it possible to eliminate elementary poles also for spin one and zero. The possibility that the physical s -wave amplitude $F_0(s)$ is not determined by the interpolation function $F_+(s, 0)$ could be used to avoid the ghost associated with the vacuum trajectory. The problem of branch-point trajectories is discussed briefly.

1. INTRODUCTION

THE possibility of describing particles as members of Regge trajectories^{1,2} in the complex angular momentum plane raises the important question whether all particles should be represented by these moving poles. As an alternative, we can envisage a description of certain particles and resonances in terms of "elementary poles"³ of the relevant amplitudes, where these poles are not related to the moving poles of the interpolating partial wave function at all. The two ways of representing particles suggest a possibility for making a qualitative distinction between "elementary" and "composite" particles. Although one may dislike such a distinction on "philosophical" grounds, it is of interest to see to what extent it may be excluded on the basis of the general notions of relativistic dispersion theory as well as specific experimental information. In this note we will be concerned mainly with strongly interacting particles, but the two ways of describing particles may

also be of interest in connection with the distinction between strong and weak interactions (and perhaps electromagnetic interactions).

In an earlier publication³ we have already described how elementary poles can be present in a physical partial wave amplitude $F_l(s)$ such that these poles are not related to a singularity of the interpolating function $F(s, \lambda)$.⁴ We have also given an argument showing that $F(s, l) = F_l(s)$ for $l > 1$, and that all particles with spin larger than one must be members of pole trajectories in the λ plane. However, this argument depends upon the existence of a Sommerfeld-Watson representation of the invariant amplitude $F(s, t)$, or a related representation which is valid for $t \rightarrow \infty$ and for some interval on the negative s axis or around $s=0$.

It is the purpose of this paper to give a more detailed description of elementary poles as compared to Regge poles within the framework of relativistic dispersion theory, and to give a more general proof for the fact that particles with spin larger than one must be manifestations of angular momentum trajectories. Furthermore, we show that any information to the effect that the high-energy limit ($t, u \rightarrow \infty$) of the invariant ampli-

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¹ T. Regge, *Nuovo Cimento* **18**, 947 (1960).

² G. F. Chew and S. C. Frautschi, *Phys. Rev. Letters* **7**, 394 (1961) and **8**, 41 (1962); R. Blankenbecler and M. L. Goldberger, *Phys. Rev.* **126**, 766 (1962); G. F. Chew, S. C. Frautschi, and S. Mandelstam, *ibid.* **126**, 1204 (1962); S. C. Frautschi, M. Gell-Mann, and F. Zachariasen, *ibid.* **126**, 2204 (1962).

³ R. Oehme, *Phys. Rev. Letters* **9**, 358 (1962).

⁴ We define here elementary poles independent of perturbation theory. For a definition within the framework of perturbation theory, see S. C. Frautschi, M. Gell-Mann, and F. Zachariasen, *Phys. Rev.* **126**, 2204 (1962); this paper contains further references.