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Uppsala University, Uppsala, Sweden

[*] Present address: Tait Institute of
Mathematical Physics, University of
Edinburgh, Edinburgh 8, Scotland

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ABSTRACT

Explicit formulas are given for the 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 preceeded 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 co-ordinates 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 energy 1) and other quantities 2) 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 $|\gamma_0(\underline{a}) - \gamma(\underline{a})|$, where $\underline{a}$ 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 Lebesque (von Neumann loc. cit.). 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 stand point. The preparatory mathematical considerations of the next section are, however, not strictly necessary for the understanding of the subsequent main discussion.

2. PRELIMINARY DIGRESSIONS

Let us consider an atomic system with N electrons and with nuclear charge Z . Let $\underline{r}_i$ and ζ_i denote the position and spin co-ordinates of the i-th electron and let x_i stand for the collection of $\underline{r}_i$ and ζ_i . The Hilbert space associated with this system will be denoted by $L_A^2(x_1, \ldots x_N)$ defined as the set of all functions $\phi(x_1, \ldots x_N)$ which are antisymmetric in the variables x_i and satisfy the condition

$$(\phi,\phi) = \int |\phi(x_1,\ldots,x_N)|^2 d\underline{r}_1 \ldots d\underline{r}_N \, d\zeta_1 \ldots d\zeta_N < \infty . \tag{1}$$

Since the set of Riemann integrable functions do not form a Hilbert space but only a linear vector space, the integration over $\underline{r}_i$ is in the sense of Lebesque, 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 space [5]) are to be considered identical. The Hamilton operator H is given in the form

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

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 Kato [6] 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

$$\int \sum_{i=1}^{N} p_i^4 \left| \tilde{\Phi}(p_1,\dots,p_N,\zeta_1,\dots,\zeta_N) \right|^2 dp_1 \dots dp_N < \infty, \tag{3}$$

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

$$(K\phi, K\phi) = \| K\phi \|^2 < \infty \tag{4}$$

where K is the kinetic energy operator. It follows from condition (3) that if $\phi \in D_H$ then $H\phi \in L_A^2$, that is, $(H\phi, H\phi) < \infty$. Following the suggestion of Kinoshita $^{7)}$ 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 $\gamma(\underline{r}_1)$ as

$$\gamma(\underline{r}_1) = \int |\Psi(x_1, x_2, \dots, x_N)|^2 d\underline{r}_2 \dots d\underline{r}_N \, d\zeta_1 \, d\zeta_2 \dots d\zeta_N \tag{5}$$

which is $\frac{1}{N}$ times the probability of finding an electron with arbitrary spin at the position $\underline{r}$. It is a consequence of a lemma by Kato (loc. cit.) that if $\psi \in D_H$ $\gamma(\underline{r}_1)$ is essentially continuous i.e. it can be made continuous by changing its value on a set of zero measure. † Here we shall be interested to estimate the quantity $|\gamma_0(\underline{a}) - \gamma(\underline{a})|$, where γ_0 is the exact density and $\underline{a}$ 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 $|\gamma_0(\underline{a}) - \gamma(\underline{a})|$ the quantity

$$\lim_{\substack{\Delta V \to 0 \\ \Delta V \ni \underline{a}}} \left| \frac{1}{\Delta V} \int_{\Delta V} \gamma_0(\underline{r}) d\underline{r} - \frac{1}{\Delta V} \int_{\Delta V} \gamma(\underline{r}) d\underline{r} \right| .$$

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

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† 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.

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 $\psi(x_1, \ldots x_N)$ be an approximate atomic wave function which satisfies conditions (1) and (3). It can always be written in the form

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

where ψ_0 is a ground state eigenfunction for the Hamilton operator given by equation (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. If ψ_0 and ψ are normalized then so is f. For typographical convenience we assume all three functions to be real. The constant η satisfies the inequality [8)]

$$\eta^2 \leqslant \frac{\lambda - E_0}{E_1 - E_0} \tag{7}$$

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

$$|(1-\eta^2)(A\psi_0,\psi_0)-(A\psi,\psi)| \leqslant \eta|(A\psi,f)+(Af,\psi)|+\eta^2|(Af,f)| \tag{8}$$

can easily be derived from equation (6) for any linear operator A. If A is self-adjoint and positive definite the identity $A = \sqrt{A}\sqrt{A}$ and Schwarz's inequality allows us to put this in the simpler form

$$|(1-\eta^2)(\psi_0,A\psi_0)-(\psi,A\psi)| \leqslant 2\eta\sqrt{(\psi,A\psi)}\sqrt{(f,Af)}+\eta^2(f,Af). \tag{9}$$

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

$$|(1-\eta^2)\gamma_0(\underline{a})-\gamma(\underline{a})| \leqslant 2\eta\sqrt{\gamma(\underline{a})}\sqrt{(\delta(\underline{a}-\underline{r}_1)f,f)}+\eta^2(\delta(\underline{a}-\underline{r}_1)f,f). \tag{10}$$

Our aim is to majorise the right hand side of inequality (10) in terms of E_0,

E_1, λ and σ, where $\sigma = \sqrt{(H\psi, H\psi) - \lambda^2}$. This will be achieved in two steps. First it will be shown that the unknown expression $[\delta(\underline{a} - \underline{r}_1)f, f]$ can be majorized in terms of (Kf, f) and (Kf, Kf) where K is the kinetic energy operator. Secondly, it can be proved that the integrals (Kf, f) and (Kf, Kf) on their turn are bounded by an expression which contains only the afore mentioned four quantities. Let us therefore consider $[\delta(\underline{a} - \underline{r}_1)f, f]$ in detail. By the definition of the δ function

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

where $g(\underline{r}_1\zeta_1, \underline{x}_2, \dots \underline{x}_N) \equiv f(\underline{r}_1 + \underline{a}, \zeta_1, \underline{x}_2, \dots \underline{x}_N)$ and $\delta(\underline{r}_1)$ is the Dirac δ in the origin. The identity

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

where $d\tau = d\underline{r}_1 \dots d\underline{r}_N d\zeta_1 \dots d\zeta_N$, can be proved by partial integration provided $\frac{d^2}{dr^2}\int g^2\, d\varphi_1 d\theta_1 d\underline{r}_2 \dots d\underline{r}_N d\zeta_1 \dots d\zeta_N$ exists everywhere except possibly on a set of isolated points. This leads to the inequality

$$\begin{aligned}|(\delta(\underline{r}_1)g, g)| &\leq \left|\frac{1}{4\pi}\int \frac{1}{r_1}\nabla_1^2 g^2 d\tau\right| = \frac{1}{2\pi}\left|\int \frac{1}{r_1} g\nabla_1^2 g\, d\tau + \right. \\ &\left. + \int \frac{1}{r_1}(\mathrm{grad}_1 g)^2 d\tau\right| \leq \frac{1}{2\pi}\left\{\left|\int \frac{1}{r_1} g\nabla_1^2 g\, d\tau\right| + \left|\int \frac{1}{r_1}(\mathrm{grad}_1 g)^2 d\tau\right|\right\}.\end{aligned} \tag{13}$$

The first term in the right hand side expression may be estimated by using Schwarz's inequality as

$$\left|\int \frac{1}{r_1} g\nabla_1^2 g\, d\tau\right| \leq \sqrt{(\nabla_1^2 f, \nabla_1^2 f)}\sqrt{\int \frac{1}{r_1^2} g^2 d\tau}\ . \tag{14}$$

On the other hand

$$\begin{aligned}\int \frac{1}{r_1^2} g^2 d\tau &= -\int g^2 \frac{\underline{r}_1}{r_1}\,\mathrm{grad}_1 \frac{1}{r_1}\, d\tau = \\ &= 2\int \frac{1}{r_1}\, g(\mathrm{grad}_1 g)\frac{\underline{r}_1}{r_1} d\tau + 2\int \frac{1}{r_1^2} g^2 d\tau\end{aligned}$$

which leads to

$$\left|\int \frac{1}{r_1^2} g^2 d\tau\right| \le \sqrt{\int \frac{1}{r_1^2} g^2 d\tau}\ \sqrt{(g, -\nabla_1^2 g)}$$

and also

$$\left|\int \frac{1}{r_1} g \nabla_1^2 g\, d\tau\right| \le \sqrt{(\nabla_1^2 g, \nabla_1^2 g)}\ \sqrt{(g, -\nabla_1^2 g)}\,. \tag{15}$$

In similar fashion one may write

$$\int \frac{1}{r_1}(\mathrm{grad}_1 g)^2 d\tau = -\int (\mathrm{grad}_1 f)\cdot\left(\frac{\underline{r}_1}{r_1}\cdot \mathrm{grad}_1\right)\mathrm{grad}_1 g\, d\tau$$

since

$$\frac{1}{2}\,\mathrm{div}\left(\frac{\underline{r}_1}{r_1}(\mathrm{grad}_1 g)^2\right) = \frac{1}{r_1}(\mathrm{grad}_1 g)^2 + \frac{\underline{r}_1}{r_1}\cdot \mathrm{grad}_1(\mathrm{grad}_1 g)^2.$$

This gives

$$\left|\int \frac{1}{r_1}(\mathrm{grad}_1 g)^2 d\tau\right| \le \sqrt{(g, -\nabla_1^2 g)}\ \sqrt{\int\left[\left(\frac{\underline{r}_1}{r_1}\cdot \mathrm{grad}_1\right)\mathrm{grad}_1 g\right]^2 d\tau}$$

and therefore

$$\left|\int \frac{1}{r_1}(\mathrm{grad}_1 g)^2 d\tau\right| \le \sqrt{(g, -\nabla_1^2 g)}\ \sqrt{(\nabla_1^2 g, \nabla_1^2 g)}\,. \tag{16}$$

Substituting inequalities (15) and (16) into (13) one obtains

$$\left|(\delta(\underline{r}_1) g, g)\right| \le \frac{3}{2\pi}\left\{(-\nabla_1^2 g, g)(\nabla_1^2 g, \nabla_1^2 g)\right\}^{\frac{1}{2}} \tag{17}$$

The Laplace operator ∇_1^2 is invariant under translation by $\underline{a}$ and therefore

$$\left|(\delta(\underline{a}-\underline{r}_1) f, f)\right| = \left|(\delta(\underline{r}_1) g, g)\right| \le \frac{3}{2\pi}\left\{(-\nabla_1^2 f, f)(\nabla_1^2 f, \nabla_1^2 f)\right\}^{\frac{1}{2}}.$$

From this it follows that

$$\left|(\delta(\underline{a}-\underline{r}_1) f, f)\right| \le \frac{3}{\pi}\frac{\sqrt{2}}{N}\left\{(Kf, f)(Kf, Kf)\right\}^{\frac{1}{2}} \tag{18}$$

since $(-\nabla_1^2 f, f) = \frac{2}{N}(Kf, f)$ and $(\nabla_1^2 f, \nabla_1^2 f) \leq \frac{4}{N}(Kf, Kf)$. The substitution of (18) into inequality (10) gives

$$|(1-\eta^2)\gamma_0(a) - \gamma(a)| \leq 2\sqrt{\gamma(a)}\left\{\frac{3}{\pi}\frac{\sqrt{2}}{N}\eta\sqrt{(Kf,f)}\,\eta\,\|Kf\|\right\}^{\frac{1}{2}} + \frac{3}{\pi}\frac{\sqrt{2}}{N}\eta\sqrt{(Kf,f)}\,\eta\,\|Kf\|. \tag{19}$$

The first part of our programme has now been accomplished. $\sqrt{(Kf, f)}$ and $\|Kf\|$ are the only unknown quantities in the right hand side expression. These can be majorized as

$$\eta\sqrt{(Kf,f)} \leq Z\sqrt{\frac{N}{2}}\,\eta + \sqrt{\frac{Z^2N}{2}\eta^2 + (\lambda - E_0) + \eta^2 E_0}, \tag{20}$$

$$\eta\|Kf\| \leq \sqrt{\sigma^2 + \lambda^2 - (1-\eta^2)E_0^2} + \sqrt{\alpha}\,\eta\sqrt{(Kf,f)} \tag{21}$$

where α is a numerical constant given by

$$\alpha = 2\left(4Z^2 + 2Z(Z-1)(N-1) + N(N-1)^2\right). \tag{22}$$

For details the reader is referred to Appendices I and II. If one introduces the notation

$$C = \frac{3}{\pi}\frac{\sqrt{2}}{N}\left(Z\sqrt{\frac{N}{2}}\eta + \sqrt{\frac{Z^2N}{2}\eta^2 + (\lambda - E_0) + \eta^2 E_0}\right) \cdot \left(\sqrt{\sigma^2 + \lambda^2 - (1-\eta^2)E_0^2} + \sqrt{\alpha}\left(Z\sqrt{\frac{N}{2}}\eta + \sqrt{\frac{Z^2N}{2}\eta^2 + (\lambda - E_0) + \eta^2 E_0}\right)\right) \tag{23}$$

it will follow from inequalities (19), (20) and (21) that

$$|(1-\eta^2)\gamma_0(a) - \gamma(a)| \leq 2\sqrt{\gamma(a)}\sqrt{C} + C \tag{24}$$

which leads to the final formula

$$|\gamma_0(a) - \gamma(a)| \leq \frac{1}{1-\eta^2}\left(2\sqrt{C}\sqrt{\gamma(a)} + C + \eta^2\gamma(a)\right) \tag{25}$$

where C is given by equation (23) and η satisfies inequality (7).

We may thus conclude that the error in the electron density $|\gamma_0(\underline{a}) - \gamma(\underline{a})|$, at any given point $\underline{a}$, is bounded by an expression which depends besides $\gamma(\underline{a})$ only on the quantities λ, σ, E_0 and η. Inequality (7) gives 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 (25) that if a sequence of trial functions converges to the exact solution i.e. $\| \psi^{(n)} - \psi_0 \| \to 0$ and if in addition $\| (H - \lambda^{(n)})\psi^{(n)} \| \to 0$, 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 $Z = \sum_{\alpha=1}^{n} Z_\alpha$, where n is the number of atoms in the system.

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

$$\gamma(\underline{a})_{spin} = \int \delta(\underline{r}_1 - \underline{a}) \psi^*(x_1, \dots, x_N) S_{z_1} \psi(x_1, \dots, x_N) dx_1 \dots dx_N$$

where the spin matrix S_{z_1} works only on the co-ordinates of electron 1. Since $\| S_{z_1} \| = \frac{1}{2}$ it can be shown by using Schwarz's inequality that

$$|\gamma_0(\underline{a})_{spin} - \gamma(\underline{a})_{spin}| \leq \frac{1}{1-\eta^2} \frac{1}{2} \left(2\sqrt{\gamma(\underline{a})}\sqrt{C} + C + \eta^2 \gamma(\underline{a}) \right)$$

where $\gamma(\underline{a})$ is again the total electron density. 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 [9]. Let therefore $\tilde{\gamma}_0(\underline{k})$ and $\tilde{\gamma}(\underline{k})$ denote the Fourier transforms of $\gamma_0(\underline{r})$ and $\gamma(\underline{r})$. By substituting $A = \frac{1}{(2\pi)^{3/2}} e^{-i\underline{k}\cdot\underline{r}}$ in inequality (8) one obtains

$$|(1-\eta^2)\tilde{\gamma}_0(\underline{k}) - \tilde{\gamma}(\underline{k})| \leq \frac{\eta}{(2\pi)^{3/2}} \left(\left|\int e^{-i\underline{k}\cdot\underline{r}} \psi f \, d\tau\right| + \left|\int e^{i\underline{k}\cdot\underline{r}} \psi f \, d\tau\right| \right) +$$

$$+ \frac{\eta^2}{(2\pi)^{3/2}} \left|\int e^{-i\underline{k}\cdot\underline{r}} f^2 d\tau\right| \leq \frac{2\eta}{(2\pi)^{3/2}} \int |\psi f| \, d\tau + \frac{\eta^2}{(2\pi)^{3/2}} \int f^2 d\tau \qquad (26)$$

and because of Schwarz's inequality this leads to

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

since ψ and f are normalized. This gives

$$\left|\tilde{\gamma}_0(\underline{k})-\tilde{\gamma}(\underline{k})\right| \leq \frac{1}{1-\eta^2}\left(\frac{1}{(2\pi)^{3/2}}(2\eta+\eta^2)+\eta^2\left|\tilde{\gamma}(\underline{k})\right|\right). \tag{27}$$

Moreover, since $|\tilde{\gamma}(\underline{k})| < \frac{1}{(2\pi)^{3/2}}\int\gamma(\underline{r})\,d\underline{r} = \frac{1}{(2\pi)^{3/2}}$ one also has the formula

$$\left|\tilde{\gamma}_0(\underline{k})-\tilde{\gamma}(\underline{k})\right| \leq \frac{2}{(2\pi)^{3/2}}\frac{\eta}{1-\eta} .$$

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 (25) by applying it to the helium atom. Since for helium Z = 2 and N = 2 we have

$$\left|\gamma_0(\underline{a})-\gamma(\underline{a})\right| \leq \frac{1}{1-\eta_{max}^2}\left(2\sqrt{C'}\sqrt{\gamma(\underline{a})}+C'+\eta_{max}^2\,\gamma(\underline{a})\right) \tag{28}$$

where

$$C \leq C' = \frac{3}{\pi}\frac{1}{\sqrt{2}}\left(2\eta_{max}+\sqrt{(4+E_0)\eta_{max}^2+(\lambda-E_0)}\right)$$

$$\left(\sqrt{\sigma^2+\lambda^2-(1-\eta_{max}^2)E_0^2}+\sqrt{44}\left(2\eta_{max}+\sqrt{(4+E_0)\eta_{max}^2+(\lambda-E_0)}\right)\right).$$

Here we made use of the fact that η^2 is bounded;

$$0 \leq \eta^2 \leq \eta_{max}^2 = \frac{\lambda-E_0}{E_1-E_0} .$$

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

It seems that inequality (28) gives sensible error limits at least for very accurate wave functions.

TABLE I. The calculated values of $2\sqrt{C'}$, C' and η^2_{max} for helium atom wave functions.

No. of parameters	$-\lambda$	σ^2	η^2_{max}	$2\sqrt{C'}$	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	0.0602	0.000 906
38	2.903 722	0.000 115	0.000 004	0.032	0.000 246

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

APPENDIX I

Upper bound for $\eta\sqrt{(Kf, f)}$

Here we shall sketch the proof of inequality (20) in section 3. From equation (6)

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

it follows that

$$\eta^2(Hf, f) = \lambda - E_0 + \eta^2 E_0 \tag{29}$$

which may be written as

$$\eta^2(Kf, f) + \eta^2(Vf, f) = \lambda - E_0 + \lambda^2 E_0, \tag{30}$$

where $V = -\sum_{i=1}^{N} \frac{Z}{r_i} + \sum_{i<j} \frac{1}{r_{ij}}$. Clearly

$$(Vf, f) \geqslant -Z\left(\sum_{i=1}^{N} \frac{1}{r_i} f, f\right)$$

and also

$$-Z\left(\sum_{i=1}^{N} \frac{1}{r_i} f, f\right) \geqslant -Z\sqrt{2N}\sqrt{(Kf, f)}.$$

For details see Kinoshita (1959) loc. cit. The substitution into equation (30) leads to

$$\eta^2(Kf, f) - \eta^2 Z\sqrt{2N}\sqrt{(Kf, f)} \leqslant \lambda - E_0 + \eta^2 E_0$$

which can be solved for $\eta\sqrt{(Kf, f)}$ to give the desired formula

$$\eta\sqrt{(Kf, f)} \leqslant Z\sqrt{\frac{N}{2}} + \sqrt{\frac{Z^2 N}{2} + (\lambda - E_0) + \eta^2 E_0}.$$

APPENDIX II

Upper bound for $\eta \| Kf \|$

As $K = H - V$,

$$\eta \| Kf \| \leqslant \eta \| Hf \| + \| Vf \| .$$

while from equation (6) it follows that

$$\eta \| Hf \| \leqslant \left\{ \sigma^2 + \lambda^2 - (1-\eta^2) E_o^2 \right\}^{\frac{1}{2}}$$

where $\sigma = \| (H - \lambda)\psi \|$. This gives

$$\eta \| Kf \| \leqslant \left\{ \sigma^2 + \lambda^2 - (1-\eta^2) E_o^2 \right\}^{\frac{1}{2}} + \eta \| Vf \| . \tag{31}$$

It remains to show that $\eta \| Vf \|$ is bounded

$$(Vf, Vf) = (V^2 f, f) = \Big(\big(-Z \sum_i \frac{1}{r_i} + \sum_{i<j} \frac{1}{r_{ij}} \big)^2 f, f \Big) =$$

$$= Z N^2 \left(\frac{1}{r_1^2} f, f \right) + Z^2 N(N-1) \left(\frac{1}{r_1} \frac{1}{r_2} f, f \right) +$$

$$+ \frac{N(N-1)}{2} \left[\left(\frac{1}{r_{12}^2} f, f \right) + 2(N-2) \left(\frac{1}{r_{12}} \frac{1}{r_{13}} f, f \right) + \frac{(N-2)(N-3)}{2} \left(\frac{1}{r_{12}} \frac{1}{r_{34}} f, f \right) \right] -$$

$$- 2Z N(N-1) \left(\frac{1}{r_1} \frac{1}{r_{12}} f, f \right) - Z N(N-1)(N-2) \left(\frac{1}{r_1} \frac{1}{r_{23}} f, f \right)$$

since f is antisymmetric in the electron co-ordinates. By dropping the term $-Z N(N - 1)(N - 2) \left(\frac{1}{r_1} \frac{1}{r_{23}} f, f \right)$ which is always negative and applying Schwarz's inequality to the three and four body terms, one obtains

$$(Vf, Vf) \leqslant Z^2 N \left(\frac{1}{r_1} f, \frac{1}{r_1} f \right) + \frac{N^2(N-1)}{4} \left(\frac{1}{r_{12}} f, \frac{1}{r_{12}} f \right) +$$

$$+ Z^2 N(N-1) \left(\frac{1}{r_1} \frac{1}{r_2} f, f \right) - 2Z N(N-1) \left(\frac{1}{r_1} \frac{1}{r_{12}} f, f \right) .$$

The last two terms cancel partly. This is a consequence of the inequality $r_{12} < r_1 + r_2$ from which it follows that $\frac{1}{r_1} \frac{1}{r_2} - \frac{1}{r_1} \frac{1}{r_{12}} - \frac{1}{r_2} \frac{1}{r_{12}} \leqslant 0$

and therefore

$$(Vf, Vf) \leq Z^2 N\left(\frac{1}{r_1}f, \frac{1}{r_1}f\right) + \frac{N^2(N-1)}{4}\left(\frac{1}{r_{12}}f, \frac{1}{r_{12}}f\right) +$$

$$+ Z(Z-1)N(N-1)\left(\frac{1}{r_1}f, \frac{1}{r_2}f\right).$$

It was shown by Kinoshita, loc. cit. (1959), that

$$\left(\frac{1}{r_1}f, \frac{1}{r_1}f\right) \leq 4\left(-\nabla_1^2 f, f\right),$$

$$\left(\frac{1}{r_{12}}f, \frac{1}{r_{12}}f\right) \leq 4\left(-\nabla_1^2 f, f\right),$$

$$\left(\frac{1}{r_1}f, \frac{1}{r_2}f\right) \leq 2\left(-\nabla_1^2 f, f\right)$$

and so one obtains

$$(Vf, Vf) \leq \alpha(Kf, f) \qquad \text{i.e.} \quad \|Vf\| \leq \sqrt{\alpha}\sqrt{(Kf, f)}$$

where $\alpha = 2\left(4Z^2 + 2Z(Z-1)(N-1) + N(N-1)^2\right)$.

Substituting this into inequality (31) the desired formula

$$\eta\|Kf\| \leq \left\{\sigma^2 + \lambda^2 - (1-\eta^2)E_0^2\right\}^{\frac{1}{2}} + \sqrt{\alpha}\,\eta\sqrt{(Kf, f)}$$

is obtained as it was shown in Appendix I that $\eta\sqrt{(Kf, f)}$ is bounded. This is a generalization of Kinoshita's formula for the many-electron case.

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