Existence of Solutions of the Hartree Equations for N Electrons An Application of the Schauder-Tychonoff Theorem

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I. Introduction. This paper will deal with the existence of solutions of the Hartree equations for N electron atoms or ions. The Hartree equations arise as an approximation to the Schrödinger equation in the following way: Each electron is assumed to move in a spherically averaged potential due to the other electrons as well as the potential due to the nucleus. Schrödinger's equation is then solved for an electron moving in such a potential, an easy task on account of the spherical symmetry. Thus, each electron is treated separately and the corresponding wave function is found with the desired quantum number. Each wave function is normalized so that the integral of the square over all space of the wave function is unity. Physically this just means that the probability of finding a particular electron somewhere in space is one. These wave functions are then used in finding the charge density arising from each electron. The total charge density due to the electrons present in the atom is then used to calculate the total potential by electrostatics. The self-consistent field requirement is then imposed; that is, the final potential must agree with the initial one which has been assumed in the Schrödinger's equation for the individual electron.

The Hartree assumptions then lead to one-electron wave functions which have the form

$$\mu_{nlm_l}(r, \theta, \varphi) = \Theta_{lm_l}(\theta)\Phi_{m_l}(\varphi)\frac{p_{nl}(r)}{r}$$

where

$$\int_0^\infty p_{nl}^2(r) dr = 1.$$

Here $\Theta_{l_i m_i}$ and Φ_{m_i} are the same as the corresponding functions which arise in the solution of Schrödinger equation for the hydrogen atom, and are normalized. The reason for this is that the separation of variables technique goes through just the same when the potential is a general function of r (due to the spherical symmetry of the averaged potential) as it does for the Coulomb potential, and the equation for the functions of θ and φ are the same as in the hydrogen atom case. Each electron in an atom is supposed to move quite independently of the others, only acted on by the others in an averaged manner. Therefore the probability density, $\bar{\psi}\psi$, where ψ is the N -electron wave function, should be a product of probability densities for the various electrons. Hence the wave function ψ should be a product of the wave functions of the individual electrons. In other words, it is assumed that the wave function is of the form

$$\begin{aligned} \psi(r_1, \theta_1, \varphi_1, \dots, r_N, \theta_N, \varphi_N) \\ = \mu_{n_1 s(1) m_{s(1)}}(r_1, \theta_1, \varphi_1) \cdots \mu_{n_N s(N) m_{s(N)}}(r_N, \theta_N, \varphi_N) \end{aligned}$$

where $s(i) = l_i$ and where the μ 's are in the form described above, each one a function of the coordinates of a single electron. The quantum numbers $n_1, l_1, m_{l_1}, \dots, n_N, l_N, m_{l_N}$ of the various electrons are assigned according to the configuration which the atom or ion to be studied is in.

With these preliminaries out of the way, the differential equations which the $p_{n_i l_i}(r)$ must satisfy can be derived. The derivation can be carried out directly by using the approximations described above, or by using a variational method. This latter method is to minimize the average energies computed by using the spherical average of the potential of an electron which underlies Hartree's approximation. This variational procedure is a satisfying method of deriving Hartree's equations, showing that they are not simply the result of intuition. This derivation of the Hartree equations can be found in [9] chapter 9. These equations are

$$(1.1) \quad \left[-\frac{d^2}{dr^2} + \frac{l_i(l_i + 1)}{r^2} - \frac{2z}{r} + \frac{2}{r} \sum_{\substack{j=1 \\ j \neq i}}^N Y_j(r) \right] p_{n_i l_i}(r) = 2\epsilon_{n_i l_i} p_{n_i l_i}(r)$$

where $1 \leq i \leq N$, and

$$Y_i(r) = \int_0^r p_{n_i l_i}^2(s) ds + r \int_r^\infty \frac{p_{n_i l_i}^2(s)}{s} ds.$$

In addition, of course, the normalizing conditions

$$(1.2) \quad \int_0^\infty p_{n_i l_i}^2(s) ds = 1$$

and boundary conditions

$$(1.3) \quad \begin{aligned} p_{n_i l_i}(0) &= 0, \\ p_{n_i l_i}(\infty) &< \infty \end{aligned}$$

must be satisfied. We note that the independent variable r in $p_{n,i,i}(r)$ is to be interpreted as r_i , the radial variable of the i^{th} electron. Here $\epsilon_{n,i,i}$ are the eigenvalues of the problem and z is the atomic number of the atom. By allowing z to be different from N we are able to treat ions as well as atoms. The inner and outer shielding (see [9]) can be taken into account by adjusting z , but here we will always consider z fixed such that $z > N - 1$. We see that the above equations can be interpreted as the Schrödinger equation for the radial part of $\mu_{n,i,s(i)m_s(i)}(r_i, \theta_i, \varphi_i)$ where $s(i) = l_i$ for an electron moving in the field of the nucleus, and all electrons other than the i^{th} , spherically averaged.

Physicists have used an iterative method of successive approximations, quite successfully, to solve these equations, but without any proof that such a scheme converges. The scheme that is used is to take the p 's determined from one stage of the approximation and use them to calculate the Y_i 's. Then insert these into the equations (1.1) and solve the linear equations (with the ϵ 's as eigenvalue parameters) for new p 's normalized by (1.2). These are used as the starting point of the next stage of approximation, calculating Y_i 's from them, and so on. Detailed techniques for actually carrying out this procedure have been described by Hartree [5].

In this paper we will not show that the above iteration scheme converges, but we will show that the operator which is defined by the above iteration scheme does have a fixed point.

There has been previous work dealing with the case of the Hartree equations for the helium atom ($N = 2$). Reeken [8] investigated the solution corresponding to the ground state of the helium atom by treating the equation as a bifurcation problem. He proved that there exists a branch of positive solutions, parameterized by the energy ϵ , which bifurcates from the lowest eigenvalue of the linearized problem and whose L_2 norm, $\|u\|$, attains the required value of 1. In order to do this, the positivity of the solution is used. In his paper Reeken leaves open the question of whether $\lim_{\epsilon \rightarrow 0-} \|u\|$ is finite or infinite. In the appendix of the present paper this question will be answered by proving that $\|u\|$ is bounded as $\epsilon \rightarrow 0-$ (for the Helium atom case $N = 2$). Gustafson and Sather [4] have also treated the Hartree equation for the helium atom as a branching problem. They prove the existence of a continuous branch of solutions in a neighborhood of the first linearized eigenvalue but do not consider whether the norm of the solutions attains the value one. However their methods treat the nonlinear partial differential equation and do not require that the equation be put in the form of an ordinary differential equation by separation variables as is done by Reeken and this author.

In the above cited work the existence question was treated as a branching or bifurcation problem since it is nonlinear. Physically this is not altogether natural since the Schrödinger equation, to which the Hartree equations are an approximation, is a linear equation and as such branching does not occur.¹ This observation has led the author in this paper to consider the existence of solutions having norm equal to one directly.

We mention also the work of Millman and Keller [7], in which are compared the solutions of the Hartree, Fock, and Schrödinger equations for the case of the Helium atom by a perturbation technique.

II. Existence of solutions. The main results can be stated as

Theorem 1. *For any set of N positive integers $\{n_1, \dots, n_N\}$ and for any set of N integers $\{l_1, \dots, l_N\}$ such that $0 \leq l_i \leq n_i - 1$, there exists a solution set $\{p_{n_1 l_1}(r), \dots, p_{n_N l_N}(r); \epsilon_{n_1 l_1}, \dots, \epsilon_{n_N l_N}\}$ of equations (1.1), where the $p_{n_i l_i}(r)$'s satisfy (1.2) and (1.3). In addition*

$$(2.1) \quad -\frac{z^2}{2n_i^2} \leq \epsilon_{n_i l_i} \leq -\frac{(z - N + 1)^2}{2n_i^2}$$

and $p_{n_i l_i}(r)$ has exactly $n_i - l_i - 1$ simple zeros on $(0, \infty)$.

The above theorem is to be interpreted physically in the following way. For a particular atom in a given state the n_i and l_i are determined by the configuration of the i^{th} electron. Or in other words n_i is the shell the i^{th} electron is in and l_i one of the energy states represented by $s, p, d, \dots$ (s corresponds to $l_i = 0$, p to $l_i = 1$, etc.) normally used by physicists. Mathematically the $\epsilon_{n_i l_i}$ can be looked upon as the n_i^{th} eigenvalue of the linear differential equation

$$\left[-\frac{d^2}{dr^2} + Q(r) \right] P = 2\epsilon P$$

together with the boundary conditions (1.2) where

$$Q(r) = \frac{l_i(l_i + 1)}{r^2} - \frac{2z}{r} + \frac{2}{r} \sum_{\substack{j=1 \\ j \neq i}}^N Y_j(r).$$

Physically $\epsilon_{n_i l_i}$ can be looked upon as minus the energy required to remove the i^{th} electron from a neutral atom. We note that the sum $\sum_{i=1}^N \epsilon_{n_i l_i}$ of the one-electron energies is *not* equal to the total energy of the atom, as might be supposed. See [9, Chap. 9] for an explanation of this point.

The proof of the above theorem is based upon showing that certain nonlinear operators (related to the Hartree iteration procedure) have fixed points. In order to define these operators, however, we will need results for the following associated linear eigenvalue problem. First we will define some sets which will be needed. Let $C^1(0, \infty)$ be the space of continuously differentiable functions on $(0, \infty)$ with the seminorm

$$\|\varphi\|_n = \max_{[1/n, n]} |\varphi| + \max_{[1/n, n]} |\varphi'|.$$

Let

$$S = \left\{ \varphi \mid \varphi \in C^1(0, \infty); 0 \leq \varphi(r) \leq N - 1; 0 \leq \varphi'(r) \leq 12z(N - 1); \right. \\ \left. |\varphi'(r_1) - \varphi'(r_2)| \leq 48z^2(N - 1) |r_1 - r_2| \right\}$$

The set S lies in the complete metric space of continuously differentiable functions on $(0, \infty)$ with the metric

$$(2.2) \quad \rho(\varphi_1, \varphi_2) = \sum_{n=2}^{\infty} \frac{\|\varphi_1 - \varphi_2\|_n}{2^n(1 + \|\varphi_1 - \varphi_2\|_n)}.$$

Call this space C ; we remark that C is a locally convex linear space.

Let L_2^1 be the Banach space of functions which are square summable on $(0, \infty)$ having a generalized derivative of first order which is also square summable on $(0, \infty)$ with

$$\|u\|_{L_2^1} = \left(\int_0^\infty u^2 ds \right)^{1/2} + \left(\int_0^\infty u'^2 ds \right)^{1/2}.$$

Let $L_{2\epsilon}^1 = \{u \mid u \in L_2^1, u \text{ is continuously differentiable on } (0, \infty)\}$.

Consider the boundary value problem

$$(2.3) \quad \frac{d^2 p}{dr^2} - \frac{l(l+1)p}{r^2} + \frac{2zp}{r} - \frac{2\varphi(r)}{r} p + 2\epsilon p = 0,$$

$$(2.4) \quad p(0) = 0, \quad p(\infty) < \infty.$$

Where ϵ is the eigenvalue parameter and $\varphi(r) \in S$.

Remark 2.1. If $p(0) = 0$ and $p \in L_{2\epsilon}^1$, then $|p(r)|$ is bounded for $r \in (0, \infty)$. Indeed

$$p^2(r) = 2 \int_0^r p(s)p'(s) ds \leq 2 \left[\int_0^\infty p^2(s) ds \right]^{1/2} \left[\int_0^\infty p'^2(s) ds \right]^{1/2}.$$

Lemma 2.1.

(a) For a fixed φ and for each positive integer j and each non-negative integer l such that $l \leq j - 1$ there exists an eigenvalue ϵ_{jl} and eigenfunction p_{jl} of equation (2.3) satisfying (2.4) where p_{jl} is twice continuously differentiable and belongs to $L_{2\epsilon}^1$.

$$(b) \quad -\frac{z^2}{2j^2} \leq \epsilon_{jl} \leq -\frac{(z - N + 1)^2}{2j^2}.$$

(c) For l fixed, ϵ_{jl} are simple eigenvalues.

(d) $p_{jl}(r)$ has exactly $j - l - 1$ simple zeros on $(0, \infty)$, such that if $\tilde{z}_{jl}^{(k)}$ is the k^{th} zero (in order of magnitude) on $(0, \infty)$ of $p_{jl}(r)$, then

$$\tilde{z}_{jl}^{(k)} \leq \tilde{z}_{jl}^{(k)} \leq \underline{z}_{jl}^{(k)},$$

where $\tilde{z}_{jl}^{(k)}$ and $\underline{z}_{jl}^{(k)}$ are the k^{th} zeros on $(0, \infty)$ of $\bar{L}_{jl}(r)$ and $L_{jl}(r)$ respectively. Here $\bar{L}_{jl}(r) = \mathfrak{L}_{j+l}^{2l+1}(2|\bar{\epsilon}_{jl}|^{1/2}r)$ and $L_{jl}(r) = \mathfrak{L}_{j+l}^{2l+1}(2|\epsilon_{jl}|^{1/2}r)$ where $\mathfrak{L}_{j+l}^{2l+1}(x)$ is the Laguerre polynomial and

$$\bar{\epsilon}_{jl} = -\frac{(z - N + 1)^2}{2j^2}, \quad l = 0, 1, \dots, j-1,$$

$$\epsilon_{jl} = -\frac{z^2}{2j^2}, \quad l = 0, 1, \dots, j-1.$$

$$(e) \quad p_{i1}(r) = O(e^{-|a_{i1}|^{1/2}r})$$

and

$$p'_{i1}(r) = O(e^{-|a_{i1}|^{1/2}r})$$

for large r .

Proof. (a) The existence of the eigenfunctions will be established by the max.min. property of eigenvalues (see [2]). Consider the following functionals on L^1_{2e} :

$$J_l(u) = \frac{\int_0^\infty u'^2(s) \, ds + l(l+1) \int_0^\infty \frac{u^2(s)}{s^2} \, ds - 2z \int_0^\infty \frac{u^2(s)}{s} \, ds + 2 \int_0^\infty \frac{\varphi(s)u^2(s)}{s} \, ds}{\int_0^\infty u^2(s) \, ds},$$

$$\bar{J}_l(u) = \frac{\int_0^\infty u'^2(s) \, ds + l(l+1) \int_0^\infty \frac{u^2(s)}{s^2} \, ds - 2(z-N+1) \int_0^\infty \frac{u^2(s)}{s} \, ds}{\int_0^\infty u^2(s) \, ds},$$

$$J_l(u) = \frac{\int_0^\infty u'^2(s) \, ds + l(l+1) \int_0^\infty \frac{u^2(s)}{s^2} \, ds - 2z \int_0^\infty \frac{u^2(s)}{s} \, ds}{\int_0^\infty u^2(s) \, ds}.$$

It is clear that since $\varphi \in S$, then

$$(2.5) \quad \bar{J}_l(u) \leq J_l(u) \leq \bar{J}_l(u).$$

Let

$$\|u\| = \left[\int_0^\infty u^2(s) \, ds \right]^{1/2} \quad \text{and} \quad (u, v) = \int_0^\infty u(s)v(s) \, ds.$$

For a functional $F(u)$ on L^1_{2e} let

$$\{F(u)\}_1 \equiv \min_{\substack{u(0)=0 \\ \|u\|=1}} F(u).$$

For $j-1$ given functions $v_1, v_2, \dots, v_{j-1}$ belonging to L^1_{2e} let

$$d\{v_1, v_2, \dots, v_{j-1}\} \equiv \min_{\substack{u(0)=0 \\ \|u\|=1 \\ (u, v_1)=0 \\ \vdots \\ (u, v_{j-1})=0}} F(u).$$

For $j \geq 2$ let

$$\{F(u)\}_i \equiv \text{maximum of } d\{v_1, v_2, \dots, v_{i-1}\}$$

where $v_1, v_2, \dots, v_{j-1}$ range over all sets of $j-1$ functions in $L^1_{2\sigma}$. By standard arguments involving the max.min. principle it can be shown that solving $\{\bar{J}_l(u)\}_i$ and $\{J_l(u)\}_i$ is equivalent to solving the two eigenvalue problems,

$$(2.6) \quad \bar{p}'' - \frac{l(l-1)}{r^2} \bar{p} + \frac{2(z-N+1)}{r} \bar{p} + 2\epsilon \bar{p} = 0, \\ \bar{p}(0) = 0, \quad \bar{p}(\infty) < \infty$$

and

$$(2.7) \quad p'' - \frac{l(l+1)}{r^2} p + \frac{2z}{r} p + 2\epsilon p = 0, \\ p(0) = 0, \quad p(\infty) < \infty,$$

respectively. These two problems can be solved explicitly for all of their eigenvalues and eigenfunctions when it is noticed that (2.7) is just the eigenvalue problem for the radial part of the wave function for the hydrogen atom. These sets of eigenvalues and normalized eigenfunctions are the following:

$$(2.8) \quad \bar{\epsilon}_{il} = -\frac{(z-N+1)^2}{2j^2}, \quad l = 0, 1, \dots, j-1, \\ \bar{p}_{il}(r) = \left(\frac{(j-l-1)!(z-N+1)}{j^2[(j+l)!]^3} \right)^{1/2} 2^{l+1} |\bar{\epsilon}_{il}|^{(l+1)/2} r^{l+1} e^{-|\bar{\epsilon}_{il}|^{1/2} r} \\ \cdot \mathfrak{L}_{j+l}^{2l+1}(2 |\bar{\epsilon}_{il}|^{1/2} r), \\ (2.9) \quad \epsilon_{il} = -\frac{z^2}{2j^2}, \quad l = 0, 1, \dots, j-1, \\ p_{il}(r) = \left(\frac{(j-l-1)!z}{j^2[(j+l)!]^3} \right)^{1/2} 2^{l+1} |\epsilon_{il}|^{(l+1)/2} r^{l+1} e^{-|\epsilon_{il}|^{1/2} r} \mathfrak{L}_{j+l}^{2l+1}(2 |\epsilon_{il}|^{1/2} r).$$

Here $\mathfrak{L}_{j+l}^{2l+1}(x)$ is the Laguerre polynomial which is described by the relations

$$\mathfrak{L}_{j+l}^{2l+1}(x) = B_0 + B_1 x + B_2 x^2 \cdots B_{j-l-1} x^{j-l-1}, \\ B_k = -B_{k-1} \frac{j-l-k}{(l+k)(l+k+1) - l(l+1)}, \\ B_{j-l-1} = (-1)^{j+l} \frac{(j+l)!}{(j-l-1)!}.$$

We therefore have

$$(2.11) \quad \{\bar{J}_l(u)\}_i = \bar{\epsilon}_{il} \quad \text{for } u = \bar{p}_{il}(r)$$

and

$$(2.12) \quad \{J_l(u)\}_i = \epsilon_{il} \quad \text{for } u = p_{il}(r).$$

Using the left side of inequality (2.5) we have that

$$(2.13) \quad -\frac{z^2}{2} = \epsilon_{10} \leq J_l(u) \quad \text{for all } u \in L_2^1$$

such that $u(0) = 0$. With this lower bound for $J_l(u)$ one can show (see [10]) that there exists a function $p_{il}(r) \in L_2^1$ with $p_{il}(0) = 0$ such that

$$\{J_l(u)\}_i = \epsilon_{il}, \quad l = 0, 1, \dots, j-1,$$

for $u = p_{il}(r)$. Using the calculus of variations it is easily shown that $p_{il}(r)$ satisfies (2.3) with $\epsilon = \epsilon_{il}$, if $p_{il}(r)$ has derivatives up to second order. $p_{il}(r)$ is continuous by virtue of it being in L_2^1 . $p'_{il}(r)$ and $p''_{il}(r)$ are continuous by the DuBois Reymond lemma of the calculus of variations (see [3] Thms. 2.4 and 2.8). Then by Remark 2.1 we have $p_{il}(\infty) < \infty$.

(b) This result follows by making use of (2.5), (2.11), and (2.12) together with a corollary of the Courant max.min. principle for eigenvalues [2].

(c) The simplicity of the eigenvalues for a fixed l follows from the fact that equation (2.3) is in the limit-point case at infinity (see [1], Chap. 9, Thm. 2.4). This guarantees that there can exist at most one non-trivial L_2^1 solution for any value of ϵ .

(d) This result follows by using part (b), and the oscillation theorem for the zeros of second order equations together with the fact that $\mathcal{L}_{i+l}^{2l+1}(x)$ has exactly $j-l-1$ zeros on $(0, \infty)$. We note that in order to apply the oscillation theorem, the behavior of $\bar{p}_{il}(r)$ and $p_{il}(r)$ near $r = 0$ must be used.

(e) These results follow directly from [6] Theorem 3.

Let S^N denote the cartesian product of S with itself N times. S^N lies in the space C^N which is the cartesian product of C with itself N times. C^N has the metric

$$\rho_N(\Psi, \Phi) = \sum_{i=1}^N \rho(\psi_i, \varphi_i)$$

where

$$\Psi = \{\psi_1, \dots, \psi_N\}$$

and

$$\Phi = \{\varphi_1, \dots, \varphi_N\}, \quad \psi_i \quad \text{and} \quad \varphi_i \in C.$$

The following lemma, which is an analogue of Arzela's theorem, will be needed in proving the compactness of certain sets in C .

Lemma 2.2. *A set K of functions in C whose elements, as well as their first derivatives, are uniformly bounded and equicontinuous on every interval $[1/k, k]$, $k \geq 2$, has a subsequence which converges (in the metric (2.2)) to an element of K .*

Proof. By applying the standard technique of using Arzela's theorem on

each interval $[1/k, k]$ and then picking convergent subsequences (in $C^1[1/k, k]$), one obtains a sequence which converges in the metric (2.2) to a function in K . In accomplishing this the following property of the metric (2.2) is used (see [11]). The sequence $\rho(\varphi_n, 0) \rightarrow 0$ if and only if $\|\varphi_n\|_k \rightarrow 0$ for each $k \geq 2$.

Lemma 2.3. S^N is compact and convex.

Proof. The compactness and convexity of S^N follows directly from the compactness and convexity, respectively, of S .

The convexity of S follows immediately from the definition of S .

The compactness of S follows directly from Lemma 2.2.

For a given set of positive integers $\{n_1, \dots, n_N\}$ and a given set of integers $\{l_1, \dots, l_N\}$ such that $0 \leq l_i \leq n_i - 1$, define the operator

$$(2.14) \quad T_{n_1 l_1, \dots, n_N l_N}(\Phi) = \Psi_{n_1 l_1, \dots, n_N l_N} = (\psi_{n_1 l_1}, \psi_{n_2 l_2}, \dots, \psi_{n_N l_N})$$

for $\Phi = (\varphi_1, \varphi_2, \dots, \varphi_N) \in S^N$, by the relations

$$(2.15) \quad \psi_{n_i l_i}(r) = \sum_{\substack{j=1 \\ j \neq i}}^N \left\{ \int_0^r p_{n_i l_i}^2(s) ds + r \int_r^\infty \frac{p_{n_i l_i}^2(s)}{s} ds \right\}$$

where $p_{n_i l_i}(r)$ satisfies

$$(2.16) \quad p_{n_i l_i}'' - \frac{l_i(l_i + 1)}{r^2} p_{n_i l_i} + \frac{2z}{r} p_{n_i l_i} - \frac{2\varphi_i}{r} p_{n_i l_i} + 2\epsilon_{n_i l_i} p_{n_i l_i} = 0,$$

$$p_{n_i l_i}(0) = 0, \quad p_{n_i l_i}(\infty) < \infty,$$

$$(2.17a) \quad \int_0^\infty p_{n_i l_i}^2(s) ds = 1,$$

and

$$(2.17b) \quad p_{n_i l_i}(r) > 0 \quad \text{for } r \in (z_{n_i l_i}^{(n_i - l_i - 1)}, \infty).$$

Lemma 2.4.

$$(2.18) \quad p_{n_i l_i}^2(r) \leq M(r) = \begin{cases} 48z^2(N-1)r, & 0 \leq r \leq \frac{1}{12z}, \\ 4z(N-1), & \frac{1}{12z} < r, \end{cases}$$

$$(2.19) \quad \int_0^\infty \frac{p_{n_i l_i}^2(s)}{s} ds \leq 12z(N-1) = A,$$

$$(2.20) \quad \int_0^\infty p_{n_i l_i}'^2(s) ds \leq 24z^2(N-1) = B.$$

Proof. We first note that

$$\int_0^\infty \frac{p_{n_i l_i}^2(s)}{s} ds < \infty$$

because of the variational characterization of $p_{n_i l_i}$. From (2.15) we have

$$(2.21) \quad \psi'_{n_i l_i}(r) = \sum_{\substack{j=1 \\ j \neq i}}^N \int_r^\infty \frac{p_{n_j l_j}^2(s)}{s} ds,$$

$$(2.22) \quad \psi''_{n_i l_i} = - \sum_{\substack{j=1 \\ j \neq i}}^N \frac{p_{n_j l_j}^2(r)}{r},$$

$$(2.23) \quad \psi_{n_i l_i}(0) = 0,$$

and

$$(2.24) \quad \psi_{n_i l_i}(\infty) = \sum_{\substack{j=1 \\ j \neq i}}^N \int_0^\infty p_{n_j l_j}^2(s) ds = N - 1,$$

using (2.17b).

From (2.21) we have $\psi'_{n_i l_i}(r) \geq 0$, so that

$$(2.25) \quad \psi_{n_i l_i}(r) \leq N - 1.$$

Also from (2.21) we have

$$(2.26) \quad \psi'_{n_i l_i}(\infty) = 0.$$

When we multiply (2.16) by $p_{n_i l_i}$ we obtain

$$\frac{1}{2}(p_{n_i l_i}^2)'' - p_{n_i l_i}'^2 - \frac{l_i(l_i + 1)}{r^2} p_{n_i l_i}^2 + \frac{2z}{r} - \frac{2\varphi_i}{r} p_{n_i l_i}^2 - 2|\epsilon_{n_i l_i}| p_{n_i l_i}^2 = 0$$

from which we have

$$(2.27) \quad (p_{n_i l_i}^2(r))'' + \frac{4z}{r} p_{n_i l_i}^2(r) \geq 2p_{n_i l_i}'^2(r)$$

and

$$(2.28) \quad \sum_{\substack{j=1 \\ j \neq i}}^N (p_{n_j l_j}^2(r))'' + \frac{4z}{r} \sum_{\substack{j=1 \\ j \neq i}}^N p_{n_j l_j}^2(r) \geq 2 \sum_{\substack{j=1 \\ j \neq i}}^N p_{n_j l_j}'^2(r).$$

Substituting (2.22) into (2.28) obtain

$$\left(\sum_{\substack{j=1 \\ j \neq i}}^N p_{n_j l_j}^2(r) - 4z\psi_{n_i l_i}(r) \right)'' \geq 2 \sum_{\substack{j=1 \\ j \neq i}}^N p_{n_j l_j}'^2(r).$$

Integrating this inequality from r to ∞ we obtain, using (2.26) and part (e) of Lemma 2.1,

$$\left(\sum_{\substack{j=1 \\ j \neq i}}^N p_{n_j l_j}^2(r) - 4z\psi_{n_i l_i}(r) \right)' \leq -2 \sum_{\substack{j=1 \\ j \neq i}}^N \int_r^\infty p_{n_j l_j}'^2(s) ds.$$

Integrating this from 0 to r and using (2.23) we have

$$(2.29) \quad \sum_{\substack{j=1 \\ j \neq i}}^N p_{n_i l_i}^2(r) - 4z \psi_{n_i l_i}(r) \leq -2 \sum_{\substack{j=1 \\ j \neq i}}^N \int_0^r \int_s^\infty p_{n_i l_i}^2(t) dt ds.$$

This inequality then implies

$$(2.30) \quad \sum_{\substack{j=1 \\ j \neq i}}^N p_{n_i l_i}^2(r) \leq 4z \psi_{n_i l_i}(r)$$

and from (2.25) we have

$$(2.31) \quad \sum_{\substack{j=1 \\ j \neq i}}^N p_{n_i l_i}^2(r) \leq 4z(N-1).$$

Therefore

$$(2.32) \quad p_{n_i l_i}^2(r) \leq 4z(N-1), \quad 1 \leq i \leq N.$$

Using (2.31) and (2.15) we have

$$\psi_{n_i l_i}(r) \leq 4z(N-1)r + r \sum_{\substack{j=1 \\ j \neq i}}^N \int_r^\infty \frac{p_{n_i l_i}^2(s)}{s} ds.$$

Combining this inequality with (2.30) we obtain

$$\frac{1}{r} \sum_{\substack{j=1 \\ j \neq i}}^N p_{n_i l_i}^2(r) \leq 16z^2(N-1) + 4z \sum_{\substack{j=1 \\ j \neq i}}^N \int_r^\infty \frac{p_{n_i l_i}^2(s)}{s} ds.$$

Integrating this from 0 to an arbitrary point b we have

$$(2.34) \quad \sum_{\substack{j=1 \\ j \neq i}}^N \int_0^b \frac{p_{n_i l_i}^2(s)}{s} ds \leq 16z^2(N-1)b + 4z \sum_{\substack{j=1 \\ j \neq i}}^N \int_0^b \int_s^\infty \frac{p_{n_i l_i}^2(t)}{t} dt ds.$$

When we integrate the integral on the right side of (2.34) by parts we obtain

$$\begin{aligned} \sum_{\substack{j=1 \\ j \neq i}}^N \int_0^b \int_s^\infty \frac{p_{n_i l_i}^2(t)}{t} dt ds &= \sum_{\substack{j=1 \\ j \neq i}}^N \left[\int_0^b p_{n_i l_i}^2(s) ds + b \int_b^\infty \frac{p_{n_i l_i}^2(s)}{s} ds \right] \\ &= \psi_{n_i l_i}(b). \end{aligned}$$

Making use of this together with (2.34) we have,

$$\begin{aligned} \sum_{\substack{j=1 \\ j \neq i}}^N \int_0^\infty \frac{p_{n_i l_i}^2(s)}{s} ds &= \sum_{\substack{j=1 \\ j \neq i}}^N \int_0^b \frac{p_{n_i l_i}^2(s)}{s} ds + \sum_{\substack{j=1 \\ j \neq i}}^N \int_b^\infty \frac{p_{n_i l_i}^2(s)}{s} ds \\ &\leq 16z^2(N-1)b + 4z \psi_{n_i l_i}(b) + \frac{1}{b} \sum_{\substack{j=1 \\ j \neq i}}^N \int_b^\infty p_{n_i l_i}^2(s) ds \\ &\leq 16z^2(N-1)b + 4z(N-1) + \frac{1}{b} (N-1). \end{aligned}$$

Therefore,

$$(2.35) \quad \sum_{\substack{i=1 \\ i \neq i}}^N \int_0^\infty \frac{p_{n_i l_i}^2(s)}{s} ds \leq \min_{0 < b < \infty} \left\{ 16z^2(N-1)b + 4z(N-1) + \frac{1}{b}(N-1) \right\} \\ = 12z(N-1).$$

This result then implies (2.19).

From (2.21) and (2.35) we have

$$(2.36) \quad \psi'_{n_i l_i}(r) = \sum_{\substack{i=1 \\ i \neq i}}^N \int_r^\infty \frac{p_{n_i l_i}^2(s)}{s} ds \leq \sum_{\substack{i=1 \\ i \neq i}}^N \int_0^\infty \frac{p_{n_i l_i}^2(s)}{s} ds \\ \leq 12z(N-1).$$

Therefore

$$(2.37) \quad \psi_{n_i l_i}(r) \leq 12z(N-1)r$$

using (2.23). Combining this inequality with (2.30) we obtain

$$\sum_{\substack{i=1 \\ i \neq i}}^N p_{n_i l_i}^2(r) \leq 48z^2(N-1)r,$$

from which we obtain

$$p_{n_i l_i}^2(r) \leq 48z^2(N-1)r, \quad 1 \leq i \leq N.$$

The last inequality combined with (2.32) gives (2.18).

Returning to (2.29) we have

$$\sum_{\substack{i=1 \\ i \neq i}}^N \int_0^r \int_s^\infty p_{n_i l_i}'^2(t) dt ds \leq 2z\psi_{n_i l_i}(r),$$

and with (2.37) one obtains

$$\int_0^r \int_s^\infty p_{n_i l_i}'^2(t) dt ds \leq 24z^2(N-1)r, \quad 1 \leq i \leq N.$$

If we integrate the integral on the left side of this last inequality by parts, we obtain

$$\int_0^r s p_{n_i l_i}'^2(s) ds + r \int_r^\infty p_{n_i l_i}'^2(s) ds \leq 24z^2(N-1)r, \quad 1 \leq i \leq N,$$

which yields

$$\int_0^\infty p_{n_i l_i}'^2(s) ds \leq 24z^2(N-1),$$

and therefore (2.20) is true.

A stronger bound than (2.18) will also be needed.

Lemma 2.5. For

$$r > R = \max \left\{ \frac{l_i(l_i + 1)}{2[z - (N - 1)]}, z_{n_i l_i}^{(n_i - l_i - 1)} \right\},$$

$$p_{n_i l_i}(r) \leq 4z(N - 1)e^{-(z - N + 1)(r - R)/n_i}.$$

Proof. We first note that for $r > R$, $p_{n_i l_i}(r) > 0$ because of (2.17b). In addition for $r > R$

$$-\frac{l_i(l_i + 1)}{r^2} + \frac{2z}{r} - \frac{2\varphi_i(r)}{r} + 2\epsilon_{n_i l_i} \geq 2\epsilon_{n_i l_i}.$$

The result follows by using the method of proof of Lemma D in the appendix of [6]. Here one uses, as the comparison differential equation, $y'' - 2|\epsilon_{n_i l_i}|y = 0$, together with parts (b) and (e) of Lemma 2.1.

Lemma 2.6. $T_{n_1 l_1, \dots, n_N l_N}$ is defined, single valued and continuous on S^N .

Proof. For simplicity $T_{n_1 l_1, \dots, n_N l_N}$ will be referred to as T . The existence of the eigenfunctions needed to define T follows from Lemma 2.1 part (a). T is single valued because of part (c) of Lemma 2.1 and (2.17a).

In order to show T is continuous, consider a sequence $\{\Phi_n\}$ in S^N which converges to Φ (which of course is in S^N). Here $\Phi_n = (\varphi_{1n}, \dots, \varphi_{Nn})$ and $\Phi = (\varphi_1, \dots, \varphi_N)$. Let $p_n = (p_{1n}, \dots, p_{Nn})$ and $\epsilon_n = (\epsilon_{1n}, \dots, \epsilon_{Nn})$ be the uniquely determined (by 2.17) eigenfunctions and eigenvalues respectively defined by Φ_n . We then have

$$T(\Phi_n) = \Psi_n = (\psi_{1n}, \dots, \psi_{Nn})$$

where

$$\psi_{in}(r) = \sum_{\substack{i=1 \\ i \neq i}}^N \left\{ \int_0^r p_{in}^2(s) ds + r \int_r^\infty \frac{p_{in}^2(s)}{s} ds \right\}.$$

Using (2.20) we have

$$(2.38) \quad |p_{in}(r_2) - p_{in}(r_1)| = \left| \int_{r_1}^{r_2} p'_{in}(s) ds \right| \leq |r_2 - r_1|^{1/2} B^{1/2}.$$

From (2.16) and (2.18) we have

$$\begin{aligned} |p''_{in}(r)| &= \left| \frac{l_i(l_i + 1)}{r^2} p_{in} - \frac{2z}{r} p_{in} + \frac{2\varphi_{in}}{r} p_{in} - 2\epsilon_{in} p_{in} \right| \\ &\leq [l_i(l_i + 1) + 2zr + 2(N - 1)r + 2z^2 r^2] \frac{M^{1/2}(r)}{r^2} \\ &\equiv \mathfrak{M}(r). \end{aligned}$$

Let $\mathfrak{M}_k = \max_{[1/k, k]} \mathfrak{M}(r)$. By the mean value theorem there exists a point

$a_{in} \in [1/k, k]$ such that

$$\left(k - \frac{1}{k}\right) p'_{in}(a_{in}) = \int_{1/k}^k p'_{in}(s) ds.$$

Therefore

$$(2.39) \quad |p'_{in}(a_{in})| \leq \left(\frac{2}{3}\right)^{1/2} B^{1/2}.$$

Also,

$$p'_{in}(r) - p'_{in}(a_{in}) = \int_{a_{in}}^r p''_{in}(s) ds, \quad r \in \left[\frac{1}{k}, k\right].$$

Therefore

$$(2.40) \quad |p'_{in}(r)| \leq \left(\frac{2}{3}\right)^{1/2} B^{1/2} + k \mathfrak{M}_k, \quad r \in \left[\frac{1}{k}, k\right].$$

Similarly we have

$$(2.41) \quad |p'_{in}(r_2) - p'_{in}(r_1)| \leq |r_2 - r_1| \mathfrak{M}_k, \quad r_1, r_2 \in [1/k, k].$$

From (2.18), (2.38), (2.40) and (2.41) we have that $p_{in}(r)$ and $p'_{in}(r)$ are uniformly bounded and equicontinuous on every interval $[1/k, k]$. Applying Lemma 2.2 and the boundedness of the ϵ_{in} from Lemma 2.1 part (b) we have the existence of subsequences $\{p_{in'}\}$ and $\{\epsilon_{in'}\}$ which converge to w_i and α_i respectively, *i.e.*,

$$\begin{aligned} \rho(p_{in'}, w_i) &\rightarrow 0 \quad \text{and} \\ |\epsilon_{in'} - \alpha_i| &\rightarrow 0 \quad \text{as } n' \rightarrow \infty. \end{aligned}$$

We use (2.16) to see that $\{p'_{in'}\}$ converges uniformly on each interval $[1/k, k]$, to a limit which must obviously be w'_i . Moreover it is easily seen that

$$w'_i - \frac{l_i(l_i + 1)}{r^2} w_i + \frac{2z}{r} w_i - \frac{2\varphi_i}{r} w_i + 2\alpha_i w_i = 0, \quad 0 < r < \infty.$$

From the fact that each $p_{in}(r)$ has exactly $n_i - l_i - 1$ zeros on $(0, \infty)$ which are bounded by part (d) of Lemma 2.1, we conclude that either w_i has at least one double zero on $(0, \infty)$ or it has exactly $n_i - l_i - 1$ zeros on $(0, \infty)$. It cannot have a double zero on $(0, \infty)$ without being identically zero since it is the solution of a second order linear equation. From the Lebesgue dominated convergence theorem and (2.17a) we have

$$\int_0^\infty w_i^2(s) ds = 1,$$

so that w_i has exactly $n_i - l_i - 1$ zeros on $(0, \infty)$. This theorem is applicable here since by (2.18) and Lemma 2.5, all the p_{in} are uniformly bounded by a function which is square integrable on $(0, \infty)$. Hence $w_i = p_i$ and $\alpha_i = \epsilon_i$, where p_i and ϵ_i are the correct eigenfunction and eigenvalue corresponding

to φ_i . Therefore picking subsequences was unnecessary and we have

$$\rho(p_{i_n}, p_i) \rightarrow 0$$

and

$$|\epsilon_{i_n} - \epsilon_i| \rightarrow 0 \quad \text{as } n \rightarrow \infty.$$

Using the Lebesgue dominated convergence theorem (again noting that the p_{i_n} are uniformly bounded by a square integrable on $(0, \infty)$) we have

$$\rho(\psi_{i_n}, \psi_i) \rightarrow 0 \quad \text{as } n \rightarrow \infty.$$

Here

$$\psi_i(r) = \sum_{\substack{i=1 \\ i \neq i}}^N \left\{ \int_0^r p_i^2(s) ds + r \int_r^\infty \frac{p_i^2(s)}{s} ds \right\},$$

and so

$$T(\Phi_n) \rightarrow \Psi = \{\psi_1, \dots, \psi_N\},$$

which shows that T is continuous.

Lemma 2.7. $T_{n_1 l_1, \dots, n_N l_N}$ maps S^N into S^N .

Proof. $T(\Phi) = \Psi = (\psi_1, \dots, \psi_N)$ lies in S^N since we will show that each ψ_i is in S . From (2.15), (2.21), and (2.24) we have that ψ_i is continuously differentiable on $(0, \infty)$ and $0 \leq \psi_i \leq N - 1$. From (2.21), (2.22) and (2.35) we have that $0 \leq \psi'_i \leq 12z(N - 1)$. From (2.22), (2.30), and (2.37) we have

$$|\psi'_i(r)| \leq 48z^2(N - 1)$$

which implies that

$$|\psi'_i(r_1) - \psi'_i(r_2)| \leq 48z^2(N - 1) |r_1 - r_2|.$$

Proof of Theorem 1. The proof is carried out by showing that the operator $T_{n_1 l_1, \dots, n_N l_N}$ has a fixed point. It is easily seen that if this operator has a fixed point in S^N , then the existence of the required solution set $\{p_{n_1 l_1}, \dots, p_{n_N l_N}; \epsilon_{n_1 l_1}, \dots, \epsilon_{n_N l_N}\}$ is assured. The $p_{n_i l_i}, \epsilon_{n_i l_i}$ will then have the required properties by using parts (b) and (d) of Lemma 2.1.

The Schauder-Tychonoff fixed point theorem will be used to prove the existence of the fixed point. This theorem states:

“A continuous mapping of a compact convex subset of a locally convex linear topological space into itself has a fixed point”.

The conditions of this theorem are satisfied by using Lemmas 2.3, 2.6, and 2.7.

Appendix. Consider the case of the ground state of the Helium atom. We have $N = 2$, $z = 2$, $l_1 = l_2 = 0$, $n_1 = n_2 = 1$, and $p_1(r) = p_2(r) = p(r)$. The

Hartree equations then reduce to

$$(A.1) \quad p'' + \frac{4}{r} p - \frac{2Q(r)}{r} p + 2\epsilon p = 0,$$

with

$$Q(r) = \int_0^r p^2(s) ds + r \int_r^\infty \frac{p^2(s)}{s} ds,$$

and boundary conditions

$$(A.2) \quad p(0) = 0, \quad p(\infty) < \infty.$$

In reference to the remark made at the end of [8], we will be interested in the behavior of solutions of (A.1) and (A.2) as $\epsilon \rightarrow 0-$.

Theorem A. *Let $p_\epsilon(r)$ be a solution of (A.1) and (A.2) with $\epsilon > 0$ and*

$$(A.3) \quad \|p_\epsilon\| = \int_0^\infty p_\epsilon^2(s) ds < \infty.$$

Then

$$(A.4) \quad \overline{\lim}_{\epsilon \rightarrow 0-} \|p_\epsilon\| \leq 4,$$

and

$$(A.5) \quad \overline{\lim}_{\epsilon \rightarrow 0-} p_\epsilon^2(r) \leq 8 \quad \text{with} \quad r \in (0, \infty).$$

Proof. We first note that (A.3) implies that $Q_\epsilon(\infty) < \infty$ and $Q_\epsilon(0) < \infty$. This implies that the behavior of $p_\epsilon(r)$ near $r = 0$ is such that

$$(A.6) \quad Q'_\epsilon(0) = \int_0^\infty \frac{p_\epsilon^2(s)}{s} ds < \infty.$$

In addition

$$(A.7) \quad \text{and} \quad \begin{aligned} p_\epsilon(r) &= O(e^{-|\epsilon|^{1/2}r}) \\ p'_\epsilon(r) &= O(e^{-|\epsilon|^{1/2}r}), \quad \text{for large } r, \end{aligned}$$

(see Lemma 2.1 part e). (A.6) implies that $Q_\epsilon(0) = 0$ and $Q'_\epsilon(\infty) = 0$.

When we multiply (A.1) by $p_\epsilon(r)$ we obtain

$$\left(\frac{p_\epsilon^2}{2}\right)'' - p_\epsilon'^2 + \frac{4}{r} p_\epsilon^2 - \frac{2Q_\epsilon}{r} p_\epsilon^2 + 2\epsilon p_\epsilon^2 = 0.$$

Replacing p_ϵ^2/r by $-Q'_\epsilon(r)$ and noting that $\epsilon < 0$ we obtain

$$(p_\epsilon^2)'' - 8Q'_\epsilon + 4Q_\epsilon Q'_\epsilon \geq 0.$$

But $Q \cdot Q'' = \frac{1}{2}(Q^2)'' - Q'^2$, so that

$$[p_*^2(r) - 8Q_*(r) + 2Q_*^2(r)]'' \geq 0.$$

We integrate this from r to ∞ and obtain

$$[p_*^2(r) - 8Q_*(r) + 2Q_*^2(r)]' \leq 0.$$

Here we have used (A.7) and $Q'_*(\infty) = 0$. We integrate again, but from 0 to r , and obtain

$$p_*^2(r) - 8Q_*(r) + 2Q_*^2(r) \leq 0.$$

This inequality can be looked upon as a quadratic inequality in $Q_*(r)$, and therefore we must have that

$$Q_*(r) \leq 4$$

and

$$p_*^2(r) \leq 8.$$

The first of these last inequalities implies (A.4) and the second implies (A.5).

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FOOTNOTE

1. The referee has pointed out to the author that in the special case of the ground state of the helium atom a solution $p(r)$ of the Hartree equation such that $\|p\| < 1$ does have a physical meaning. By the use of proper scaling factors of the variable r and a solution $p(r)$, it can be shown that a solution of arbitrary norm $\|p\|$ for a fixed charge z corresponds to a solution having norm equal to 1 for a charge $z\|p\|^{-2}$ and a different eigenvalue. This implies that the author's proof (see appendix) that the Hartree equation for helium does not have solutions of arbitrarily large norm, means that this model of an atom becomes unstable when the charge of the nucleus is decreased to zero. This fact, as the referee mentions, is to be expected from physical intuition.

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